Inorg. Chem. **2004**, *43*, 1545–1550

Inorganic Chemistry

Article

Easy Preparation of the Tris(2-fluoro-6-pyridylmethyl)amine Ligand and Instantaneous Reaction of the Corresponding Dichloroferrous Complex with Molecular Dioxygen: New Access to Dinuclear Species

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Received May 9, 2003

The tris(2-fluoro-6-pyridylmethyl)amine ligand, F_3TPA, can easily be prepared by reaction of 2-fluoro-6-bromomethylpyridine with NH_4Cl in the presence of NaOH. Complexation to $FeCl_2$ affords the high-spin $F_3TPAFe^{(II)}Cl_2$ complex, the X-ray structure of which is reported. The three fluorine substituents provide enough steric hindrance to force the tripod to coordinate in the tridentate mode, affording a trigonal bipyramidal iron center. This complex is thermally stable, and it reacts instantaneously with molecular dioxygen to afford the unsymmetrical μ-oxo dimer $F_3TPAFe^{(III)}ClOFe^{(III)}Cl_3$ as the major product, together with small amounts of the mixed salt $[F_3TPAFe^{(II)}Cl]_2$, $[Fe^{(III)}_2OCl_6]$. These two complexes have been isolated and characterized by X-ray diffraction analysis. A mechanism by which they are obtained is suggested and seems to parallel the well-known process of autoxidation of ferrous porphyrins.

Introduction

The chemistry of iron complexes with ligands of tris(2-pyridylmethyl)amine type (TPA) has undergone a fantastic expansion during the past decade.[1] One of the main reasons for this is that many TPA-containing complexes have been used as synthetic analogues of the active sites of some mono- or dimetallic non-heme metalloproteins for which dioxygen activation is involved.[2,3] Among the stable oxidation states of iron, ferrous is obviously the most appropriate for the study of oxygen ligation at the molecular level. In fact, most of the catalytic studies involving iron TPA complexes are dominated by the use of the so-called "shunt reaction", for which already reduced forms of dioxygen, (hydro)peroxides, react with ferric or ferrous states, whereas in the oxygen dependent process, nature uses molecular dioxygen together with ferrous sites.[4−10] Recent reports indicate that the field of dioxygen ligation and activation by di-iron TPA complexes is rapidly expanding.[11] However, studies of the mononuclear species still need more development. With mononuclear systems, some work has been reported in which catecholate or (α-keto)carboxylate bound ferrous derivatives in the TPA series react quickly with dioxygen: these particular complexes thus qualify as models for catechol

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10.1021/ic034485e CCC: $27.50

dioxygenases or α-ketoglutarate-dependent dioxygenases.[12−14] Rapid reaction of dioxygen with thiolate bound complexes has also been described.[15] In fact, in the absence of bound reactive ligand, coordination of O_2 generally occurs at much lower rates.

With respect to catalysis in oxidation, it appears that the most extensively studied complexes are those with the parent TPA ligand or its methylated or acylated analogues in 5 or 6 position. We followed the naïve idea that the introduction of halogens as electron withdrawing groups might increase the oxidative power of the catalysts when high-valent metal oxo species are involved. We thus investigated the preparation of some fluorinated tripods, with a special emphasis on the α-fluorinated tris(2-fluoro-6-pyridylmethyl)amine (F_3-TPA), the synthesis of which to our knowledge had not been reported in the literature. Indeed, we found that its preparation is surprisingly simple and straightforward. We then noticed that the corresponding dichloroferrous monomeric complex **1**, $F_3TPAFe^{(II)}Cl_2$, reacts instantaneously with molecular dioxygen in the absence of any bound substrate to afford the unsymmetrical μ-oxo dimmer **2** $F_3TPAFe^{(III)}ClOFe^{(III)}Cl_3$, together with small amounts of the mixed salt **3** $[F_3TPAFe^{(II)}Cl]_2$, $[Fe^{(III)}{}_2OCl_6]$. In this article, we have two goals. The first is to report the easy preparation of the ligand F_3-TPA, together with the X-ray crystal structure of its dichloroferrous complex; the second is to demonstrate that within the thoroughly investigated chemistry of the iron−TPA complexes, the very important class of μ-oxo dimers can be easily accessed, simply from ferrous derivatives and dry molecular dioxygen. All complexes mentioned in this article are structurally characterized.

Experimental Section

^{1}H NMR data were recorded in CD_3CN ($CDCl_3$ for the ligand and precursor) at ambient temperature on a Bruker AC 300 spectrometer at 300.1300 MHz using the residual signal of CD_2HCN ($CHCl_3$) as a reference for calibration. ^{19}F NMR data were recorded on the same spectrometer in CH_3CN at 282.4045 MHz using the signal of $CFCl_3$ as reference for calibration.

The UV−vis spectra were recorded on a Varian Cary 05 E UV−vis−NIR spectrophotometer.

Conductivity measurements were carried out under argon at 20 °C with a CDM 210 Radiometer Copenhagen conductivity meter, using a Tacussel CDC745-9 electrode.

Elemental analyses were carried out by the Service Central d'Analyses du CNRS in Vernaison, France.

2-Fluoro-6-bromomethyl Pyridine. A 5 g (45 mmol) portion of the commercially available 2-fluoro-6-methyl pyridine was dissolved in 200 mL of CCl_4. A 9 g (51 mmol) portion of NBS was added, and the medium was refluxed for 6 h in the presence of 300 mg of benzoyl peroxide. The solvent was then evaporated and the solid extracted with toluene. The concentrated toluene solution was chromatographed on silica gel using toluene as eluent and the desired compound collected as the second fraction. Evaporation of the solvent yielded 1.95 g (23%) of a pale yellow oil. Anal. C_6H_5NBrF Calcd %: C, 37.89; H, 2.63. Found %: C, 37.60; H, 2.21. ^{1}H NMR, δ, ppm, $CDCl_3$: 7.78, 1H, dd, $^3J^{HH} = 8.05$ Hz, $^3J^{HF} = 7.05$ Hz; 7.30, 1H, dd, $^3J^{HH} = 7.32$ Hz, $^5J^{HF} = 2.20$ Hz; 6.85, 1H, dd, $^3J^{HH} = 8.23$ Hz, $^4J^{HF} = 2.74$ Hz; 4.44, 2H, s. ^{19}F NMR, δ, ppm, $CDCl_3$: −66.88, $^3J^{FH} = 7.05$ Hz.

Preparation of F_3TPA. 2-Fluoro-6-bromomethyl pyridine (1.3 g, 6.84 mmol) was suspended with NH_4Cl (130 mg, 2.43 mmol) in a mixture THF/H_2O 90:10 (150 mL). The pH was adjusted to 10 by addition of aqueous NaOH. The resulting medium was stirred 4 days at room temperature in a tightly closed flask. The reaction mixture was then poured into CH_2Cl_2 and the organic phase separated, washed with water, and then dried by $MgSO_4$. Addition of cold *n*-hexane to the cold concentrated solution afforded white crystals of F_3TPA, which were dried under vacuum. A 940 mg (40%) yield of microcrystalline material could thus be recovered. The crystallization mother solution only contained the starting 2-fluoro-6-bromomethyl pyridine, which can be recovered by rotary evaporation and used in another cycle. Anal. $C_{18}H_{15}N_4F_3$ Calcd %: C, 62.79; H, 4.36. Found %: C, 62.91; H, 4.21. ^{1}H NMR, δ, ppm, $CDCl_3$: 7.69, 3H, dd, $^3J^{HH} = 7.31$ Hz, $^3J^{HF} = 8.25$ Hz; 7.39, 3H, dd, $^3J^{HH} = 8.05$ Hz, $^5J^{HF} = 2.60$ Hz; 6.72, 3H, dd, $^3J^{HH} = 7.32$ Hz, $^4J^{HF} = 2.10$ Hz; 3.78, 6H, s. ^{19}F NMR, δ, ppm, $CDCl_3$: −67.93, $^3J^{FH} = 8.25$ Hz. (Further information about ^{19}F−^{1}H couplings can be found in J. B. Rowbotham et al. *Can. J. Chem.* **1971**, *49*, 1799, and ref 1 quoted by these authors).

Metalation of F_3TPA was carried out according to the already published procedure.[18] Analytical data for **1** follow. Anal. $C_{18}H_{15}Cl_2F_3FeN_4$ Calcd %: C, 45.86; H, 3.18. Found %: C, 45.61; H, 2.92. MSES$^+$: $m/z = 435.2$ (**1** − Cl^-).

Oxygenation of 1. Crystals of **2** and **3** were grown by layering the oxygenated acetonitrile solutions of **1** with dry and degassed diethyl ether in stopped or sealed crystallization tubes. Mainly brown crystals of **2** were obtained, together with some orange crystals of **3**. Preparative scale: 100 mg of 1 were dissolved in ca. 150 mL of degassed CH_3CN, and dry dioxygen was bubbled for 5 s. The orange-brown solution was immediately concentrated to half volume, and upon bulk addition of diethyl ether, a brown solid was obtained. It was washed with diethyl ether (or THF) to remove the free ligand released, which was identified by ^{1}H NMR. Further workup yielded two fractions containing **3** and **2**.

(i) Extraction of the solid with acetonitrile followed by ether (or THF) precipitation allowed us to obtain small amounts of compound **3** as a dark solid. The amount of solid was just enough to allow characterization by elemental analysis (C and H), NMR, and MS. Analytical data follow. Anal. $C_{36}H_{30}Cl_8F_6Fe_4N_8O$ Calcd %: C, 35.64; H, 2.47. Found: C, 35.24; H, 2.05. MSES$^+$: no molecular ion signal, detection of (**1** − Cl^-) at $m/z = 435.2$ as result of the dissociation of the dication. Compound **3** was also characterized by its ^{1}H NMR and UV−vis spectra, both given as Supporting Information. After data collection, the NMR tubes were layered with diethyl ether. Since **3** crystallizes easily, single crystals were thus obtained which displayed the same parameters as those obtained from crystallization experiments.

(ii) The CH_3CN low solubility fraction yielded 50 mg of **2**, obtained as a dark brown powder (77% with respect to **1**).

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Compound **2** was characterized by elemental analysis, mass spectroscopy, and UV−vis spectroscopy. ^{1}H NMR spectroscopy displayed weak signals within the 20−0 ppm range. **2**: $C_{18}H_{15}Cl_4F_3Fe_2N_4O$. Anal. Calcd %: C, 35.18; H, 2.44; N, 9.12. Found %: C, 35.10; H, 2.11; N, 8.65. MSES$^+$: $m/z = 578.1$ ($\mathbf{2} - Cl^-$), $m/z = 542.9$ ($\mathbf{2} - 2Cl^-$).

X-ray Analysis. Single crystals of **1**, **2**, and **3** were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα $\lambda = 0.71073$ Å). Quantitative data were obtained at 173 K for **1** and **3** and 183 K for **2**. The complete conditions of data collection (Denzo software) and structure refinements are given in the Supporting Information section. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in φ angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software (*Kappa CCD Operation Manual*; Nonius B. V.: Delft, The Netherlands, 1997. Sheldrick, G. M. *SHELXL97, Program for the refinement of crystal structures*; University of Gottingen: Germany, 1997). The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Crystal data for **1**: yellow crystals, monoclinic, space group $P2_1/c$, $a = 8.7940(10)$ Å, $b = 12.8111(10)$ Å, $c = 17.2910(10)$ Å, $\beta = 94.9660(10)°$, $V = 1940.7(3)$ Å^3, $D_{calcd} = 1.612$ g·cm^{-3}, $Z = 4$. For 8505 unique, observed reflections with $I > 2\sigma(I)$ and 253 parameters, the discrepancy indices are $R = 0.046$ and $R_w = 0.113$.

Crystal data for **2**: brown crystals, monoclinic, space group $P2_1/n$, $a = 10.641(5)$ Å, $b = 18.559(5)$ Å, $c = 11.676(5)$ Å, $\beta = 95.097(5)°$, $V = 2296.7(16)$ Å^3, $D_{calcd} = 1.769$ g·cm^{-3}, $Z = 4$. For 6699 unique, observed reflections with $I > 2\sigma(I)$ and 289 parameters, the discrepancy indices are $R = 0.046$ and $R_w = 0.137$.

Crystal data for **3**: orange crystals, triclinic, space group $P\bar{1}$, $a = 9.343(5)$ Å, $b = 9.569(5)$ Å, $c = 13.696(5)$ Å, $\alpha = 102.621(5)°$, $\beta = 93.289(5)°$, $\gamma = 105.610(5)°$, $V = 1142.0(10)$ Å^3, $D_{calcd} = 1.762$ g·cm^{-3}, $Z = 2$. For 5172 unique, observed reflections with $I > 2\sigma(I)$ and 286 parameters, the discrepancy indices are $R = 0.083$ and $R_w = 0.129$.

Results and Discussion

The preparation of the tri-α bromo substituted TPA has already been reported[16] and involves, from the starting 2-bromo-6-bromomethylpyridine, three steps including several separations with an overall yield of 36%. Although this procedure might certainly be applicable to the fluorinated derivative, we tried the direct condensation of 2-fluoro-6-bromomethylpyridine with NH_4Cl in a 3:1 stoichiometric ratio in the presence of NaOH and obtained F_3TPA as a microcrystalline powder with a yield of 40% of analytically pure compound,[17] without any need for chromatographic separation. Although this is a moderate yield, the reaction is clean and requires only one step as displayed in Figure 1. The convenience of the preparation together with the fact that the only side product recovered is the unreacted 2-fluoro-6-bromomethyl pyridine makes this procedure quite attractive. Metalation of F_3TPA was achieved by standard methods[18] and yielded the dichloroferrous complex $F_3TPAFe^{(II)}Cl_2$ **1** in semiquantitative yield as a yellow thermally stable solid. Slow diffusion of dry and degassed diethyl ether in anaerobic acetonitrile solution of **1** afforded crystals suitable for X-ray diffraction analysis.

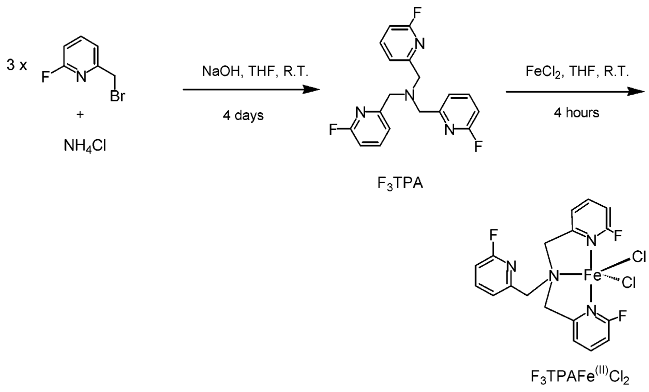

Figure 1. Preparation of F_3TPA and the corresponding dichloroferrous complex **1**.

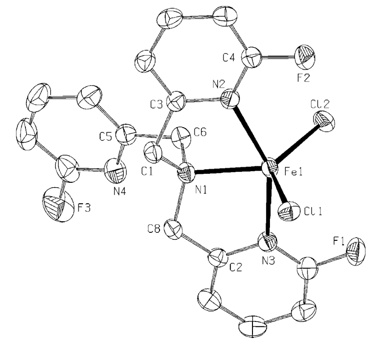

Figure 2. ORTEP diagram of compound **1** showing a partial numbering scheme. The hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Fe−Cl1 = 2.306(1), Fe−Cl2 = 2.311(1), Fe−N1 = 2.186(1), Fe−N2 = 2.267(1), Fe−N3 = 2.234(1), Cl2−Fe−Cl1 = 130.9(1), N2−Fe−N3 = 152.3(1), N2−Fe−N1 = 75.6(1), N3−Fe−N1 = 77.0(1).

The ORTEP diagram of **1**, shown in Figure 2, reveals a distorted trigonal bipyramidal geometry around the metal, with one fluoropyridine arm remote from the coordination site. This structure is very similar to those that we already reported in some dichloroferrous complexes with bis α-substituted TPA ligands.[18] A tridentate coordination mode of the ligand to $FeCl_2$ is indeed known to result from ligand disubstitution with bulky groups (Br or phenyl substituents). In the present case, the same effect is induced by trisubstitution, which compensates for the fact that the fluorines are smaller than other halides. Indeed, short distances of 3.36 and 3.58 Å are found between Cl2 and the fluorine atoms of the ligand. Tetradentate coordination would certainly afford a less stable species. The ligand to metal distances are indicative of a high spin state of the metal in this complex[19,20] with values for d_{Fe-N} all above 2.1 Å. The distortion from the ideal bipyramidal geometry confirms the flexibility of the ligand [∠N2−Fe−N1 = 76.95(7)°, ∠N3−Fe−N1 = 75.59(7)°, and ∠N2−Fe−N3 = 152.28(7)°, for instance]. The τ index is in the present case equals to $\tau = 0.36$, i.e., indicative of a noticeable distortion with respect to the ideal TBP geometry in **1**.[21] The question of the conservation of the structure in solution for related complexes

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has already been addressed by using various spectroscopic techniques: indeed, a careful examination of the UV−vis, molecular conductivity, and ^{1}H NMR data yields in general useful information.[18] The UV−vis spectrum of **1** is dominated by a strong ligand-centered transition at $\lambda = 261$ nm ($\epsilon = 8.05$, 10^3 mmol·cm^2), the lack of any other noticeable absorption supporting a tridentate coordination mode of the tripod. In acetonitrile, **1** displays a molecular electric conductivity value $\chi = 41$ S·cm^2·mol^{-1}, which indicates that the complex remains neutral in solution. This observation rules out any possibility of iron−chloride dissociation. The ^{1}H NMR spectrum displays broad resonances within the 70−30 ppm range and looks qualitatively similar to that obtained from dichloroferrous complexes with the TBP geometry.[18] ^{19}F NMR of **1** is of great help in the present case. Two signals are observed at $\delta = 45.2$ ppm ($\Delta\nu_{1/2} = 961$ Hz), i.e., paramagnetically shifted and strongly broadened, and $\delta = -70.3$ ppm ($\Delta\nu_{1/2} = 92$ Hz), in the diamagnetic region and significantly broadened. The first corresponds to the fluorine atoms of the bound pyridines, strongly affected since they are located in α position of the coordinated nitrogen. Within the diamagnetic region and with a significant broadening, the second is assigned to the fluorine atom from the dangling arm. Thus taken together, these observations demonstrate that the structure of the complex as seen in the solid state is retained in solution.

Upon exposure to analytical grade dry dioxygen, the yellow CH_3CN solution of **1** immediately changed to brown. The UV−vis spectrum of the medium indicated the presence of new absorptions at $\lambda = 312$ and 358 nm, which were further assigned to the formation of compound **2**. Slow diffusion of dry diethyl ether to this solution afforded crystals of two distinguishable types. Brown crystals of **2** were obtained as the main material, together with orange crystals of compound **3** obtained in minor amounts. Both types of crystals could be studied by X-ray diffraction, and their structures are reported. Alternatively, addition of a large excess of diethyl ether to the oxygenated medium allowed precipitation of a brown powder, consisting of **2** mainly, together with traces amounts of **3**. On the basis of solubility properties, separation of **3** from the medium was possible.

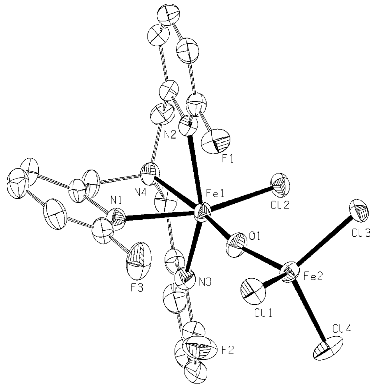

Figure 3. ORTEP diagram of compound **2** showing a partial numbering scheme. The hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Fe1−Cl2 = 2.310(1), Fe1−O1 = 1.757(2), Fe1−N1 = 2.252(3), Fe1−N2 = 2.226(3), Fe1−N3 = 2.177(3), Fe1−N4 = 2.240(3), Fe2−O1 = 1.754(2), Fe2−Cl1 = 2.239(1), Fe2−Cl3 = 2.261(1), Fe2−Cl4 = 2.248(1), Fe1−Fe2 = 3.464(2), N2−Fe1−N3 = 149.3(1), N1−Fe1−Cl2 = 164.4(1), N4−Fe1−O1 = 173.7(1), Fe1−O1−Fe2 = 161.3(1).

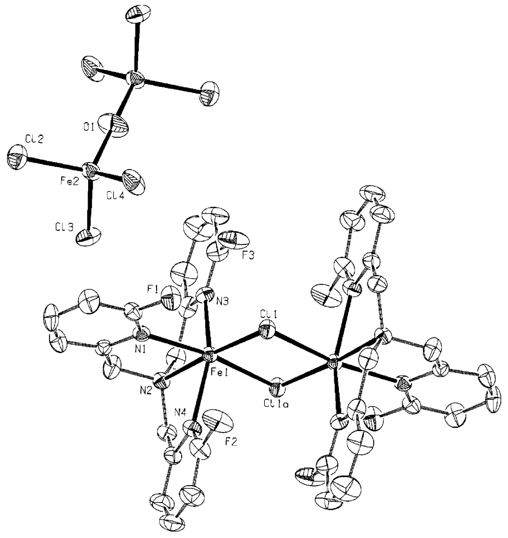

Figure 4. ORTEP diagram of compound **3** showing a partial numbering scheme. The hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Fe1−Cl1 = 2.350(1), Fe1−Cl1a = 2.553(1), Fe1−N1 = 2.194(4), Fe1−N2 = 2.222(4), Fe1−N3 = 2.221(4), Fe1−N4 = 2.245(4), Fe1−Fe1′ = 3.547(4), Fe1−Cl1−Fe1′ = 92.6(1), Cl1−Fe1−Cl1′ = 87.5(1), N1−Fe1−Cl1′ = 166.5(1), N2−Fe1−Cl1 = 174.5(1), N3−Fe1−N4 = 151.3(1).

Compound **2**, whose ORTEP diagram is displayed in Figure 3, is the unsymmetrical μ-oxo dinuclear complex $F_3TPAFe^{(III)}ClOFe^{(III)}Cl_3$. In this compound, the presence of only one chloride bound to the metal in the iron-tripod fragment decreases the steric hindrance around the metal, the shortest fluorine−chloride distance being now *d*F1−Cl2 = 4.43 Å. Thus, tetradentate coordination of F_3TPA is allowed, with a distorted octahedral geometry around Fe1. The Fe1−N as well as the Fe1−Cl distances all lie in the expected range for high-spin ferric derivatives.[22,23] On the other hand, Fe2 is tetrahedrally coordinated and bound to Fe1 by a bridging oxygen atom. Unlike in previously described structures of unsymmetrical iron μ-oxo complexes,[22,24] the metal oxo distances are equivalent with *d*Fe1−O1 = 1.757(2) Å and *d*Fe2−O1 = 1.754(2) Å, and no specific elongation of the N4−Fe1 bond trans to the oxo ligand is observed. The distortion from linearity, expressed by the ∠Fe1−O−Fe2 angle of 161.23(15)° is moderate, and the Fe1−Fe2 distance of 3.464(2) Å lies in the expected range. Finally, noteworthy is the fact that all three fluoride atoms are in close contact with the bridging oxo group, with an average F−O1 distance of 2.90 Å.

Compound **3** is the mixed salt $[F_3TPAFe^{(II)}Cl]_2$, $[Fe^{(III)}{}_2OCl_6]$. Its ORTEP diagram is displayed in Figure 4. The dication $[F_3TPAFe^{(II)}Cl]_2{}^{2+}$ displays the well-known bis(μ-halo)di-iron core structure that has already been reported with the tris(3,5-dimethyl-1-pyrazolylmethyl)amine, tris(6-methyl-

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2-pyridyl)amine, and TPA ligands.[25] The cation in compound **3** has an inversion center, and the two bridging chlorides bind to each iron unsymmetrically. The tripod acts as a tetradentate ligand, and each iron adopts a distorted octahedral environment. Again, the metal-to-ligand distances support a high spin state for each iron in the complex. The Fe−Fe separation is 3.547(4) Å and can be compared with the 3.494(3) Å value found in $[TPAFe^{(II)}Cl]_2^{2+}$.[25] Also, the ∠FeClFe = 92.59(3)° angle is slightly higher than the value of 90.67(3)° found in $[TPAFe^{(II)}Cl]_2^{2+}$, and this small difference certainly reflects the steric effect of α-trisubstitution of the tripode by a fluorine atom. Furthermore, the Fe_2Cl_2 core imposes the angle ∠ClFeCl = 87.41(3)°, i.e., more acute than the ∠ClFeCl in **1**, and a slight lateral shift of the ligand becomes possible without breaking the molecular structure, allowing tetradentate coordination of F_3TPA. Indeed, one chloride only is facing the cavity defined by the fluorine atoms of the tripod. The corresponding average distance is dF−Cl1 = 3.1(2) Å, whereas the shortest distance to the other chloride is dF−Cl1a = 4.566(2) Å. Thus, steric hindrance is not too severe in **3**. Finally, in the counteranion $Fe_2Cl_6O^{2-}$, the metal is tetrahedral with a linear FeOFe segment, and unlike in the reported pyridinium salt,[26] it exhibits a staggered conformation.

The poor solubility of **2** made it difficult to obtain ^1H NMR spectra with a good signal-to-noise ratio. We could only notice that all detectable signals appeared within the compact 20−0 ppm range; the UV−vis spectrum of **2** exhibited one ligand centered absorption at $\lambda = 262$ nm ($\epsilon = 8.93$, 10^3 mmol·cm^2) together with absorptions at $\lambda = 312$ and 358 nm ($\epsilon = 1.45$ and 1.05 10^3 mmol·cm^2, respectively) typical for μ-oxo species. By contrast, **3** is more soluble and displays paramagnetically shifted signals between $\delta = 40$ and $\delta = 60$ ppm. A single broad resonance is observed in its ^{19}F NMR spectrum at $\delta = -69.8$ ppm ($\Delta\nu_{1/2} = 530$ Hz), confirming that all fluorine atoms are equivalent in solution. The UV−vis spectrum of **3** consists of three absorptions at $\lambda = 262$, 308, and 356 nm ($\epsilon = 5.58$, 2.50, and 1.62×10^3 mmol·cm^2, respectively). All traces are given as Supporting Information. We thus believe that the properties of **2** and **3** in solution are very likely to be similar to those of the related μ-oxo or bis-(μ-halo) complexes for which antiferromagnetic or ferromagnetic exchange interaction between the iron atoms, respectively, has been reported.[22,24,25]

μ-Oxo dinuclear ferric complexes are well-known in the chemistry of TPA[27] and are generally obtained from water solvated ferric salts and ligands in the presence of polar solvents. Unsymmetrical derivatives are more unusual, and except for one complex briefly mentioned in a recent article with a tetradentate ligand, they are all obtained from ferric salts.[22,24,28,29] Compound **1** is perfectly stable and can be kept in solution at room temperature for several weeks without alteration, in a tightly closed vessel. However, **1** is sensitive to dioxygen and reacts within a fraction of second to yield **2** together with minor amounts of **3**. The geometry around the metal in **1** is probably one of the reasons for such a sensitivity, although it might not be the only cause.[30] Generation of μ-oxo derivatives by action of molecular dioxygen on ferrous compounds, the so-called "autoxidation mechanism", is well-known in the chemistry of porphyrins.[31] A similar pathway has been invoked to explain the final formation of a thiolate bound ferric derivative with thiolate bound TPA ferrous complexes.[15] In our case, we have no substrate likely to bind nor activate the metal, and the standard "autoxidation" pathway is very likely to be the only possible route to μ-oxo derivatives from O_2 and a mononuclear complex. In the already reported unsymmetrical derivatives, the values for the Fe−Fe separation are 3.456(2) and 3.411(1) Å.[22,24] In $TPAFe^{(III)}ClOFe^{(III)}ClTPA$, distances of 3.581(2) and 3.565(2) Å have been reported.[27,32] Considering that our starting material contains ligands somehow hindered by fluorine atoms and that μ-oxo formation is the driving force, the conservation of the Fe−O−Fe segment may simply require decoordination of one of the two tripods, leading to the unsymmetrical derivative **2** with a short distance of 3.464(2) Å. The mechanism by which minor amounts of **3** are formed is more speculative. We believe that within the reaction conditions (some decomposition and polar medium obtained under these conditions), the chloride ions in **1** dissociate and combine with inorganic fragments to yield **3** as the mixed salt.

Considering the cation $[F_3TPAFe^{(II)}Cl]_2^{2+}$ from a structural point of view, due to a slightly longer metal to metal distance in the Fe_2Cl_2 core than in **2**, and because the bulkiness of the fluorine substituents remains modest, decoordination of one of the ligand would simply be not necessary to afford a stable complex.

A general tentative mechanism is shown in Scheme 1.[33]

In conclusion, we have reported a very convenient preparation of the tris(2-fluoro-6-pyridylmethyl)amine ligand F_3TPA, which was unknown. The small fluorine atoms provide enough steric hindrance to restrain coordination of the tripod to $FeCl_2$ to the tridentate mode and to decoordinate

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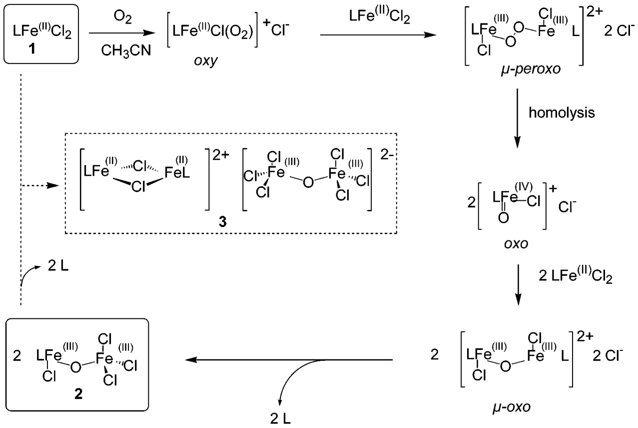
(33) This mechanism is corroborated by the fact that only 25% molar equivalent of O_2 with respect to **1** is necessary to observe complete disappearance of **1** by ^{1}NMR. Details: 100 mg of **1** (0.21 mmol) was dissolved in ca. 150 mL of degassed CH_3CN and stirred under strict argon atmosphere. A 1.2 mL (0.05 mmol) portion of dry dioxygen was introduced to the medium via a gastight syringe. The medium was kept under strict argon atmosphere for 1 h and the solvent removed under vacuum. The ^1H NMR spectrum of the resulting brown solid, sampled under strict anaerobic conditions, showed complete disappearance of **1**. The spectrum showed evidence of the presence of **2**, and small amounts of **3**, together with trace amounts of extra paramagnetic signals.

Scheme 1. Adaptation of the Autoxidation Mechanism[a] to the Chemistry of O_2-Sensitive Ferrous TPA Complexes, Showing a Putative Reaction Pathway Leading to the Formation of **2** and **3**



[a] See ref 31. The dashed frame and line indicate that only small amounts of **3** are obtained.

one metal in the μ-oxo derivative. However, this steric hindrance is not as important as breaking of the symmetry in dinuclear systems containing the Fe_2Cl_2 core. Also, we have shown that the dichloroferrous complex reacts immediately with dioxygen in the absence of exogenous biomimetic ligands. This is unprecedented in the chemistry of mononuclear iron TPA complexes. We thus provide an example of simple access to the very important class of μ-oxo diferric derivatives, the structure of one unsymmetrical complex being described. Our results strongly suggest that the autoxidation mechanism, postulated in chemistry of porphyrins 25 years ago, is also valid for more simple derivatives. Understanding the parameters that govern the sensitivity to dioxygen requires insights into electrochemical properties and geometrical considerations within a series of related complexes. Together with the study of the conditions which might allow trapping and identification of the postulated intermediates, these points are under investigation in our laboratory.

Acknowledgment. The authors thank the CNRS and ULP for financial support.

Supporting Information Available: ^1H NMR and ^{19}F NMR traces for 2-fluoro-6-bromomethyl pyridine, F_3TPA free ligand, and compounds **1** and **3**. UV−vis traces for compounds **1**, **2**, and **3**. UV−vis trace of a solution of **1** recorded 30 s after oxygenation. For the three reported structures, crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034485E