measurements and Mark Schure for valuable discussions. M. A.E.-S. and A.E.-T. thank Alexandria University for study leave.

## Appendix

Consider a fixed molecular core geometry with *m* equivalent sites, each of which can be occupied by any one of *n* different metals. The number of possible metal stoichiometries is given by eq A1. The total number of discrete molecules, *N*, depends

$$s = \frac{(n + m - 1)!}{m!(n - 1)!} \qquad \text{(A1)}$$

on the core geometry. Examples: (1) $N = 24$ when $n = 4$ for the trinuclear core structures VA and VB (Table V); (2) $N = 36$ when $n = 4$ for the tetrahedral core structure III (Table VI).

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# Preparation and Characterization of a Binuclear Iron-$\mu$-Dioxygen Complex: $[(Ph_3PO)_4FeOOFe(OPPh_3)_4{\cdot}2H_2O](ClO_4)_4$

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*Received June 29, 1988*

The combination of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ with HOOH, $m$-$ClC_6H_4C(O)OOH$, $Me_3COOH$, PhIO, $PhI(OAc)_2$, $Bu_4N(IO_4)$, $O_3$, or NaOCl in anhydrous acetonitrile results in the formation of the binuclear complex $[(Ph_3PO)_4FeOOFe(OPPh_3)_4{\cdot}2H_2O](ClO_4)_4$ (**1**). The same material is produced from the addition of HOOH plus two $^-OH$ ions to $[Fe^{III}(Ph_3PO)_4](ClO_4)_3$ in acetonitrile. The complex has been characterized by elemental analysis, electronic, vibrational, and ESR spectroscopy, solid- and solution-phase magnetic susceptibility measurements, and electrochemistry. Mechanistic pathways are proposed for the formation of **1** and for its reactivity with halide ions.

Hydrogen peroxide and related oxygen atom donors are activated by $Fe^{II}(MeCN)_4{}^{2+}$ in anhydrous acetonitrile.[1,2] The resulting systems mimic the substrate transformations by enzymes such as catalase,[3] peroxidase,[4] and cytochrome P-450[5] and appear to involve a reactive iron(II)–oxene, $[Fe^{II}(O)]^{2+}$.[6] The present report describes the unique chemistry that results when triphenylphosphine ($PPh_3$) is the substrate for the $[Fe^{II}(MeCN)_4]^{2+}/H_2O_2/MeCN$ system.

The *slow* introduction of HOOH to an MeCN solution that contains $Fe^{II}(MeCN)_4(ClO_4)_2$ and $PPh_3$ causes the substrate to be converted to triphenylphosphine oxide ($Ph_3PO$), with the iron remaining as Fe(II) (consistent with the reactivity for other substrates).[1,2] However, the *rapid addition* of HOOH to the same system results in the formation of a deep purple complex (**1**), which is identical with that formed by the addition of HOOH (or other oxygen atom donors such as PhIO, $O_3$, $m$-$ClPhC(O)OOH$, $IO_4{}^-$, and $^-OCl$) to an MeCN solution that contains $[Fe^{II}(OPPh_3)_4](ClO_4)_2$. The same complex is formed by the addition of HOOH plus two $^-OH$ to $[Fe^{III}(OPPh_3)_4](ClO_4)_3$. The purple product (**1**) has been isolated and characterized, and its reactivity investigated in relation to the activation of HOOH by $[Fe^{II}(MeCN)_4]^{2+}$ in acetonitrile.

## Experimental Section

**Equipment.** The resonance Raman spectra were recorded with the optics in a 90° scattering configuration on a computer-controlled Spex Industries Ramalog 6 spectrometer equipped with a thermoelectrically cooled Hamamatsu R955 photomultiplier tube and a photon-counting detection system. Excitation at 488 nm was provided by an argon ion laser (Coherent Innova 15). Resonance Raman spectra were collected at 2-$cm^{-1}$ intervals (0.5 s/point). The incident laser power was between 50 and 75 mW, and the spectral slit width was approximately 3 $cm^{-1}$. The spectra were recorded for solid samples prepared in KCl pellets (20 mg/200 mg of KCl) and MeCN solutions (20–40 mM) sealed in a glass capillary tube.

Diffuse-reflectance infrared (DRIFT) spectra were run on a Nicolet 60-SX FTIR spectrometer equipped with a Barnes diffuse-reflectance attachment and a wide-range mercury–cadmium telluride detector. The spectra were collected at 4-$cm^{-1}$ resolution for 500 scans. Samples were run either in synthetic diamond (20 $\mu$m, Kay Industrial Diamond Corp.) or KCl. Conventional IR spectra were recorded of solid samples prepared in KCl pellets on a Perkin-Elmer Model 283B spectrometer (spectral resolution 2 $cm^{-1}$).

A Cary Model 219 spectrophotometer and a Hewlett-Packard Model 8451 diode-array spectrophotometer were used for the UV–visible spectrophotometric measurements.

The solution-phase magnetic susceptibility measurements were made with Varian EM-390 and XL-200 NMR spectrometers by the Evans method[7] (as modified by Rettig[8]) and made use of the paramagnetic shift of the methyl protons of TMS (added as an internal standard). Solid-state magnetic susceptibility data were obtained with a variable-temperature superconducting susceptometer/magnetometer system (SQUID).[9] Pascal constants were used for diamagnetic corrections.[10]

The ESR spectra were recorded with a Bruker Model 200 X-band spectrometer equipped with an Oxford Instruments liquid-helium cryostat and temperature controller for low-temperature measurements. Liquid-nitrogen ESR spectra (77 K) were obtained by immersing the sample tubes in a liquid-nitrogen finger Dewar that was placed within the ESR cavity.

A three-electrode potentiostat (Bioanalytical Systems Model CV-1 or CV-27) and a Houston Instruments Model 100 Omnigraphic X-Y recorder were used for the cyclic voltammetric experiments. Controlled-potential coulometric electrolysis was accomplished with either a Princeton Applied Research Model 173/179 potentiostat/digital coulometer or a Bioanalytical Systems Model CV-27 potentiostat.

A Bioanalytical Systems microcell assembly was adapted to use a glassy-carbon working electrode, a platinum-flag auxiliary electrode, and a Ag/AgCl reference electrode filled with aqueous tetraethylammonium chloride solution and adjusted to 0.000 V vs SCE.[11] The latter was contained in a Pyrex tube with a soft-glass cracked tip; this electrode was placed inside a luggin capillary that contained the MeCN electrolyte solution. The cell was closed with a Teflon cap that included holes for

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**Table I.** Products, Yields, and Analytical Data for the Production of **1** via the Use of Different Oxygenating Agents[a]

| oxygenating agent | yield[b] of **1**, % | % C | % H | % P | % Fe | % O | other products[c] (yield, %)[d] |
|---|---|---|---|---|---|---|---|
| HOOH | 56.1[e] | 61.2 | 4.4 | 8.6 | 4.2 | 15.6 | |
| $m$-$ClC_6H_4C(O)OOH$ | 93.0 | 61.0 | 4.4 | 8.4 | 4.0 | 15.5 | $m$-$ClC_6H_4C(O)OH$ (100) |
| PhIO | 87.2 | 59.6 | 4.3 | 8.3 | 4.0 | 15.3 | PhI (87.3) |
| $PhI(OAc)_2$ | 85.1 | | | | | | PhI (94.9) |
| **1**[f] | | 61.7 | 4.5 | 8.8 | 4.0 | 16.0 | |

[a] A 5-fold excess of oxygenating agent was combined with 1 equiv of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ in dry acetonitrile. Reaction times: HOOH, 2 h; all others, 30 min. [b] Based on $[Fe^{II}(OPPh_3)_4](ClO_4)_2$. [c] Identified by gas chromatography. [d] Based on standard solutions. [e] The low yield of **1** for this reacton was the result of insufficient reaction time ($H_2O_2$ requires several hours to achieve complete production of **1**). [f] Calculated for $[(Ph_3PO)_4FeOOFe(OPPh_3)_4 \cdot 2H_2O](ClO_4)_4$.

deaeration by high-impurity argon and for sample introduction.

The organic products from both the synthesis and the substrate reactions were separated and identified with a Hewlett-Packard Model 8550A gas chromatograph that was equipped with a 12.5-m glass capillary column.

Ozone ($O_3$) was generated with a Welsbach Laboratory Ozonator, Model T-408.

**Reagents.** Acetonitrile (MeCN) (Burdick and Jackson Laboratories "distilled in glass", <0.004% $H_2O$) was used for all the studies and syntheses. Tetraethylammonium perchlorate (TEAP) (G. Frederick Smith Co.) was used as the supporting electrolyte in the electrochemical studies and was vacuum-line-dried for at least 24 h prior to use. Tetramethylammonium superoxide, $(Me_4N)O_2$, was prepared by either combination of $KO_2$ and $(Me_4N)OH \cdot 5H_2O$ and subsequent extraction in liquid ammonia[12] or by the electrochemical reduction of an MeCN solution through which oxygen (at 1 atm) was continuously bubbled. $[Fe^{II}(OPPh_3)_4](ClO_4)_2$,[13] $[Fe^{III}(OPPh_3)_4](ClO_4)_3$,[13] and PhIO[14] were prepared as described in the literature. Labeled ($^{18}O$) iodosobenzene was prepared[15] and used to synthesize labeled complex **1**. Pure HOOH (assay >98%) was prepared by vacuum distillation of 30% HOOH (J. T. Baker). $Me_3COOH$ (Aldrich, 3.0 M, in toluene), $PhI(OAc)_2$ (Aldrich), $Bu_4NIO_4$ (Aldrich), and $m$-$ClC_6H_4C(O)OOH$ (Aldrich; available peracid was assayed by iodometry) were used as oxygen atom transfer reagents. Commercially available 5% NaOCl solution (Chlorox) also was used as a source of oxygen atoms. All other reagents and solvents were highest purity available, and were used as received.

**Methods.** The cyclic voltammograms were initiated at the rest potential of the solution, and all voltages are reported vs SCE. All of the solutions contained 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte and were characterized at 24 ± 1 °C.

Spectrophotomeric titrations (stoichiometric studies) were accomplished by adding a known volume of a standard solution of either the oxygenating agent or the halide to a 10-mL volumetric flask that contained a known volume and concentration of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$, $[Fe^{III}(OPPh_3)_4](ClO_4)_3$, or **1**, and then diluting to the mark with MeCN. Alternatively, successive 1-$\mu$L injections of a standard solution of either the oxygenating agent or halide were made into a solution that contained a known volume and concentration of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ or **1**. The absorbance of the latter solution, which was contained in a cylindrical quartz spectrophotometer cell, was measured after each injection at the maximum for **1** (576 nm).

Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, TN.

The system for the study of substrate reactivity consisted of a 30-mL glass reaction cell with 0.05 mmol of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ and 1.0 mmol of substrate in 10 mL of MeCN. To this vigorously stirred solution was added 1.0 mmol of HOOH (98%) in 10 mL of MeCN over a several-minute period. The resulting product solution was extracted with diethyl ether and dried over $MgSO_4$, and the extract was analyzed by gas chromatography.

**Synthesis of $[(Ph_3PO)_4FeOOFe(OPPh_3)_4 \cdot 2HOH](ClO_4)_4$ (1).** After 1.0 g (0.74 mmol) of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ was dissolved in 30 mL of dry MeCN, a 5-fold excess of the oxygenating agent was added (either neat or as a solution in 10 mL of dry MeCN) over a period of 60 s (the formation of **1** is exothermic). The original pale yellow solution rapidly became deep purple and was allowed to stir for 30 min. With hydrogen peroxide (98%) as the oxygenating agent the reaction required several hours for completion. The product solution was slowly added to 1 L of diethyl ether to precipitate a deep purple product, which was collected by suction filtration, washed several times with diethyl ether, and then dried in vacuo for several days over $BaSO_4$ or $P_2O_5$. The yield was usually >80% based on $[Fe^{II}(OPPh_3)_4](ClO_4)_2$. The isolated product did not exhibit any adverse effects upon exposure to the atmosphere, both as a solid and as a solution in MeCN, $CHCl_3$, $CH_2Cl_2$, $(CH_3)_2CO$, and $C_6H_6$. Solid samples of **1** showed no appreciable decomposition after several months storage in a desiccator. Table I summarizes the yields and elemental analyses for the production of **1** from several syntheses that made use of different oxygenation agents. The stoichiometric combination of two $[Fe^{III}(OPPh_3)_4](ClO_4)_3$, one HOOH, and two $^-OH$ in MeCN also was used to produce **1**.

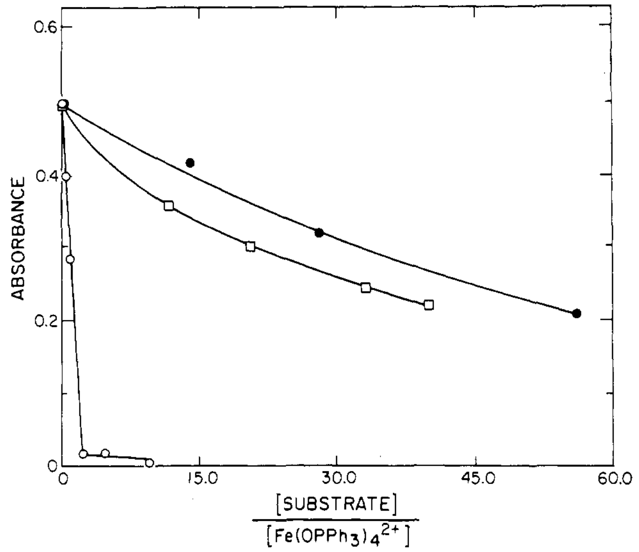

**Figure 1.** Effect of organic substrates upon the yield of **1** for the reaction of a 2- or 3-fold excess of HOOH per $Fe^{II}(OPPh_3)_4^{2+}$ (0.3 mM) in MeCN: (○) $PPh_3$; (□) $Ph_2SO$; (●) cyclohexene. The absorbance at 576 nm ($\epsilon$ 3.54 $mM^{-1}$ $cm^{-1}$) is characteristic of **1** and the yield is close to stoichiometric in the absence of organic substrates.

## Results

**Formation of $[(Ph_3PO)_4FeOOFe(Ph_3PO)_4 \cdot 2H_2O](ClO_4)_4$ (1).** The reaction stoichiometry for the preparation of **1** in dry MeCN[16] is approximately 1 equiv of oxygenating agent/$[Fe^{II}(OPPh_3)_4](ClO_4)_2$; the mole ratio for HOOH is 1.10 ± 0.14, that for $m$-$ClC_6H_4C(O)OOH$ is 1.05 ± 0.30, and that for PhIO is 0.82 ± 0.16. The maximum production of **1** requires that the iron(II) be coordinated by four $Ph_3PO$ ligands. The product solutions also contain the deoxygenated form of the oxygenating agent in >85% yield (Table I). On the basis of the electronic spectra for the product solutions, the addition of $Me_3COOH$, $PhI(OAc)_2$, $Bu_4N(IO_4)$, $O_3$, or NaOCl to a dry MeCN solution that contains $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ also results in the formation of **1**. However, the systems are complicated by side reactions and variable reaction stoichiometries. In the case of NaOCl, **1** is formed initially, but subsequently reacts with the liberated $Cl^-$ or $OH^-$ that is present in the NaOCl solution. Addition of NaOCN to $Fe^{II}(OPPh_3)_4(ClO_4)_2$ does not yield **1**. The complex may form transiently before

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(16) Complex **1** also can be prepared in dry solutions of $CH_2Cl_2$, THF, and $(CH_3)_2CO$.

**Table II.** Products and Conversion Efficiencies for the $[Fe^{II}(OPPh_3)_4](ClO_4)_2$-Induced Monooxygenation of Organic Substrates (RH) by HOOH in Dry Acetonitrile[a]

| substrate (RH) | reaction efficiency,[b,c] % | products |
|---|---|---|
| $PPh_3$ | 100 | $OPPh_3$ |
| $Ph_2SO$ | 55 | $Ph_2SO_2$ |
| 1-hexene | 6 | 1-hexene oxide[d] |

[a] At 0 °C; to 1.0 mmol of substrate and 0.5 mmol of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ in 10–20 mL of MeCN was added slowly 1.0–1.5 mmol of HOOH (1 M HOOH in MeCN). [b] Based on $Fe^{II}(OPPh_3)_4(ClO_4)_2$. [c] Within the time frame of the experiment (30–45 min) and in the absence of $[Fe^{II}(OPPh_3)_4](ClO_4)_2$, HOOH did not react significantly with either solvent or substrate. [d] Based on a 3% yield of 2,5-dibutyl-1,4-dioxane. The production of dioxanes from epoxides is catalyzed by the presence of strong Lewis acids such as $Fe^{III}$ complexes (see ref 17).

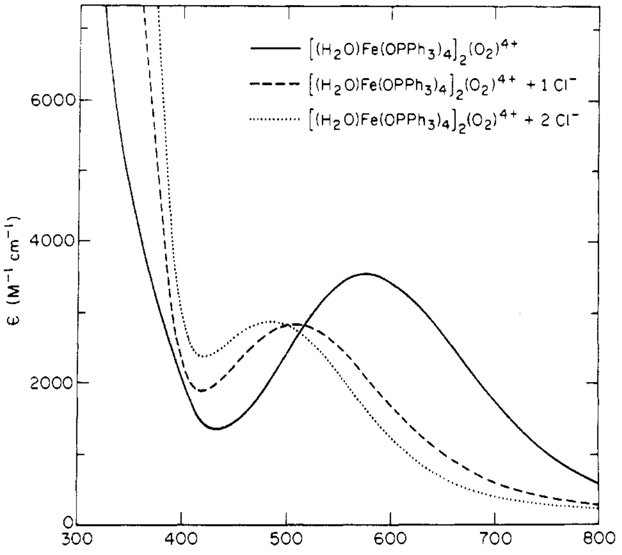

**Figure 2.** Absorption spectra in MeCN for 1 mM solutions of **1** (prepared from *m*-$ClC_6H_4C(O)OOH$) in the presence of (a) no added $Cl^-$, (b) 1 equiv of $Cl^-$, and (c) 2 equiv of $Cl^-$.

it is rapidly destroyed by the liberated $CN^-$.

The yield of **1** is greatly diminished when the formation reaction is done in the presence of organic substrates (RH). Figure 1 illustrates this for various mole ratios of $PPh_3$, $Ph_2SO$, and cyclohexene, and Table II summarizes the extent that these substrates are monooxygenated by the reaction intermediates from the combination of $Fe^{II}(OPPh_3)_4{}^{2+}$ and a 2- or 3-fold excess of HOOH.[17]

The addition of HOOH to an MeCN solution that contains $[Fe^{III}(OPPh_3)_4](ClO_4)_3$ yields **1** with a rate of formation that is first order in $[Fe^{III}]$ and [HOOH]. The rate is enhanced by the presence of $H_2O$ (or $^-OH$) and reaches a maximum for 10 mM $H_2O$ (0.28 mM Fe(III) and 2.8 mM HOOH). Analysis of the kinetic data (absorbance at 576 nm vs. time) for the latter conditions yields a value of 0.047 ± 0.005 $M^{-1}$ $s^{-1}$ for the apparent second-order rate constant. With larger concentrations of $H_2O$, molecular oxygen is evolved with the production of a wine red (530 nm) solution [in contrast to the purple color (576 nm) of **1**].

Combination of $O_2{}^{\bullet -}$ [electrochemically generated or from $(Me_4N)O_2$] with either $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ or $[Fe^{III}(OPPh_3)_4](ClO_4)_3$ fails to produce **1** as a primary product. If an oxygen-saturated MeCN solution that contains $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ is allowed to stand for several weeks, the solution gradually turns purple (the presence of **1** is confirmed by UV–visible spectroscopy).

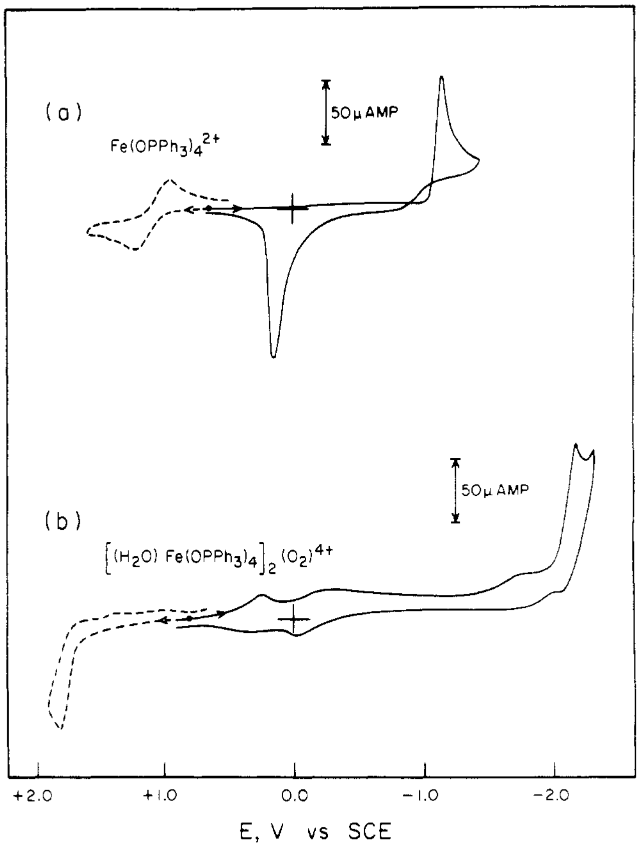

**Figure 3.** Cyclic voltammograms in MeCN for (a) 3 mM $Fe^{II}(OPPh_3)_4(ClO_4)_2$ and (b) 1.5 mM **1** (prepared from PhIO). Scan rate = 0.1 V $s^{-1}$; glassy-carbon working electrode (area 0.11 $cm^2$).

**Physical Characterization of 1.** Figure 2 illustrates the UV–visible spectrum for complex **1** in MeCN, which is dominated by a broad ligand-to-metal charge-transfer band [$\lambda_{max}$ = 576 nm ($\epsilon$ = 3.54 $mM^{-1}$ $cm^{-1}$)] that is absent from the spectrum for $[Fe^{II}(OPPh_3)_4](ClO_4)_2$. The Raman spectra for **1** in MeCN and for **1** as a solid in KCl are identical, with unique vibrational bands at 882, 565, and 445 $cm^{-1}$ at an excitation wavelength of 488.0 nm; the 882-$cm^{-1}$ band is not present in the IR spectrum for **1**. If **1** is prepared from $PhI^{18}O$ this band shifts to 848 $cm^{-1}$. These bands are not present in the Raman spectra for $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ and $[Fe^{III}(OPPh_3)_4](ClO_4)_3$. The infrared spectrum of **1** exhibits unique bands at 1455 and 1268 $cm^{-1}$ that are absent in the IR spectra for $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ and $[Fe^{III}(OPPh_3)_4](ClO_4)_3$.

The average magnetic moment of **1** is 5.83 ± 0.50 $\mu_B$/iron on the basis of solution-phase measurements (Evans' method).[7] The solid-phase magnetic moment of **1** decreases from 5.95 $\mu_B$/iron at 300 K to 5.22 $\mu_B$ at 6 K (a plot of $(1/\chi_M)_{cor}$ vs $T$ is linear with a $\theta$ value of 0.15). Liquid-nitrogen ESR spectra for polycrystalline samples of **1** exhibit a broad signal centered at $g$ = 4.2. The signal and its intensity are closely similar to those recorded for $[Fe^{III}(Ph_3PO)_4](ClO_4)_3$ with equivalent instrument settings and concentration.

Cyclic voltammograms for $[Fe^{II}(OPPh_3)_4](ClO_4)_2$ and for **1** are illustrated in Figure 3. The purple complex (**1**) exhibits a major irreversible reduction peak at −2.1 V vs SCE and a major irreversible oxidation peak at +1.93 V (the reduction peaks at +0.28, −0.14, and −1.8 V vs SCE are due to dissociation products of **1** and residual PhIO, respectively).

**Reactivity of 1.** Complex **1** does not react when combined with substrates such as $PPh_3$, $Ph_2SO$, $PhCH_2OH$, PhCH(O), and cyclohexene and is quantitatively recovered (even under forcing conditions or elevated temperatures and extended reaction times). Strong Lewis bases such as $^-OH$ and pyridine react with **1** (stoichiometry, 2 equiv of base/**1**); the starting complex is recovered upon addition of $H^+$. However, the addition of either excess $^-OH$ or $H^+$ irreversibly destroys **1**. With $^-OH$ this de-

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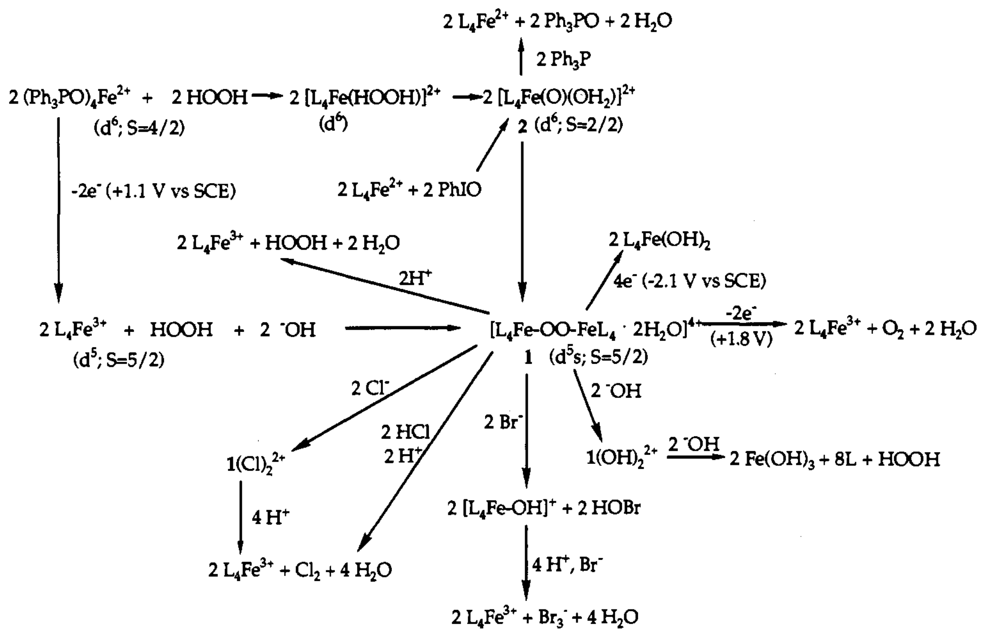
[17] Sugimoto, H.; Sawyer, D. T. *J. Org. Chem.* **1985**, *50*, 1784.

**Scheme I**



composition reaction is rapid, but the reaction of excess protons requires several hours for completion.

Tetraalkylammonium bromides and iodides as well as HCl, HBr, and HI react with **1** (2:1 stoichiometry) to produce $\mathrm{Fe^{III}(OPPh_3)_4}^{3+}$ and $X_2/X_3^-$ (demonstrated by UV–visible spectroscopy; some halide adducts of $\mathrm{Fe^{III}(OPPh_3)_4}^{3+}$ also are formed). The chemistry appears to be analogous to that for the catalyzed oxidation of halides by $H_2O_2$ ($2HX + HOOH \rightarrow X_2 + 2H_2O$).[18] However, the combination of $Me_4NCl$ with **1** results in a ligand-addition reaction. A spectrophotometric titration of **1** with $Cl^-$ in the absence of $H^+$ exhibits two inflection points at mole ratios of 1:1 and 2:1 $Cl^-$:**1**. The absorption spectra for the two adducts are illustrated in Figure 2. Addition of excess $Cl^-$ causes the eventual decomposition of **1**.

Addition of **1** to PhC≡CPh and cyclohexane (each in a pyridine/acetic acid solvent matrix) results in their transformation to PhC(O)C(O)Ph (3% yield based on 1:1 stoichiometry) and cyclohexanone (5% yield), respectively (as the only significant products).[19]

## Discussion and Conclusions

The stoichiometric studies establish that 2 mol of oxygenating agent and 2 mol of $[\mathrm{Fe^{II}(OPPh_3)_4}](\mathrm{ClO_4})_2$ are required to produce 1 mol of **1**.[20] The Raman spectrum for **1** confirms the presence of a dioxygen linkage, with the band at 882 cm$^{-1}$ assigned to the O–O stretch. This is consistent with other peroxo transition-metal complexes[21] and with the O–O stretch for HOOH in the liquid phase (877 cm$^{-1}$).[22] The 34-cm$^{-1}$ shift (882 cm$^{-1}$ → 848 cm$^{-1}$) for the $^{18}$O-labeled complex also is in accord with this assignment. The presence of a single line for the labeled compound indicates the complete incorporation of $^{18}$O (from the oxygenating agent, PhI$^{18}$O) into the dioxygen group of the complex. The absence of a corresponding band at 882 cm$^{-1}$ in the IR spectrum for **1** indicates a symmetric environment for the dioxygen group, and the absence of bands near 1100 and 1550 cm$^{-1}$ eliminate superoxide ion or dioxygen as terminal ligands in the complex.

The unique IR bands at 1268 and 1455 cm$^{-1}$ for **1** appear to be the result of geometric changes experienced by the four $Ph_3PO$ ligands upon formation of **1** from $[\mathrm{Fe^{II}(OPPh_3)_4}](\mathrm{ClO_4})_2$. In the latter they are tetrahedrally arranged about the metal center, but in **1** they most likely form a square plane about the metal.

The magnetic susceptibility and ESR data indicate that the two metal centers of **1** are high-spin d$^5$s iron and are magnetically independent of each other at room temperature. The decrease in magnetic moment at lower temperature may indicate weak antiferromagnetic coupling between the two metal centers or selective population of Kramers doublets for the high-spin iron centers. In agreement with the magnetic susceptibility data, the ESR signal at $g = 4.2$ for **1** is characteristic of high-spin iron in a rhombic environment.

The electrochemistry of **1** is dominated by the irreversible reduction peak at −2.1 V vs SCE and the irreversible oxidation peak at +1.8 V vs SCE, which are similar to those observed for free HOOH in MeCN (−1.8 V vs SCE and +2.1 V vs SCE, respectively).[23]

The intense purple color (576 nm, Figure 2) of complex **1** is characteristic of a charge-transfer band. A similar absorption band ($\lambda_{max} = 505$ nm) is observed for an iron(III)–EDTA–peroxo complex.[21a]

**Mechanism for the Formation of 1.** The results in the preceding section and the stoichiometry for the formation of **1** from $[\mathrm{Fe^{II}(OPPh_3)_4}](\mathrm{ClO_4})_2$ and the various oxygenating agents in MeCN are in accord with a mechanism that is analogous to that for the $\mathrm{Fe^{II}(MeCN)_4}^{2+}$/HOOH system.[1,2] The initial step is the formation of an Fe$^{II}$–oxene intermediate.

$$\underset{(d^6;\ S = 4/2)}{2[\mathrm{Fe^{II}(Ph_3PO)_4}]^{2+}} + 2\mathrm{R'(O)} \rightarrow \underset{\mathbf{2}\ (d^6;\ S = 2/2)}{2[(\mathrm{Ph_3PO})_4\mathrm{Fe^{II}(O)}]^{2+}} + 2\mathrm{R'} \tag{1}$$

R′(O) = HOOH, $m$-ClPhC(O)OOH, $Me_3COOH$, PhIO, PhI(OAc)$_2$, $Bu_4N(IO_4)$, $O_3$, NaOCl

The observed reactivity of an intermediate from the $[\mathrm{Fe^{II}(OPPh_3)}]^{2+}$/HOOH combination with organic substrates (Figure 1 and Table II) indicates that it has "Fe$^{II}$–oxene-like" properties (**2**, eq 1).

In the absence of substrate, species **2** dimerizes to give the purple complex (**1**, Scheme I). Such a dimerization process is consistent

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with the complete incorporation of $^{18}O$ into the product when the monooxygen atom donor $PhI^{18}O$ is used. The high-spin $d^5s$ formulation for the valence electrons of the iron centers is supported by the electrochemical and magnetic measurements. The product from the combination of $(Cl_8TPP)Fe^+$ and $^-OH$, $(Cl_8TPP)Fe\text{-}OH$, has a magnetic moment of 5.5 $\mu_B$, which is consistent with $d^5sp^2$ valence-electron hybridization.[24] The assignment of the Raman band at 882 $cm^{-1}$ to a dioxygen bridge (FeOOFe) is supported by the $^{18}O$-labeling experiment and the similarity of the band to that for free HOOH (877 $cm^{-1}$).[22] Likewise, the electrochemical oxidation at +1.8 V vs SCE is closely similar to that for HOOH in MeCN ($\mathbf{1} \xrightarrow{-2e^-} 2L_4Fe^{3+} + O_2 + 2HOH$). The potential shift of +0.7 V (from the +1.1 V value for the $L_4Fe^{2+}/L_4Fe^{3+}$ couple) is a measure of the covalent-bond formation energy for $[L_4Fe\text{–}OOFeL_4]^{4+}$ $[(-\Delta G)_{BF} = 0.7 \times 23.1 = 16\ \text{kcal}]$.[25] Because $(-\Delta G)_{BF}$ for the H–OOH bond is about 80 kcal, the $[L_4FeO\text{–}OFeL_4]^{4+}$ bond energy should be substantially greater than that for the HO–OH bond ($\Delta H_{BDE} = 51$ kcal).[26] Addition of excess $^-OH$ to **1** induces its rapid decomposition to $Fe(OH)_3$ and HOOH, which is consistent with these estimated bond energies.

Additional support for the formulation of **1** is provided by its stoichiometric synthesis from the combination of 2 mol of $[Fe^{III}(Ph_3PO)_4](ClO_4)_3$ with 1 mol of HOOH plus 2 mol of $^-OH$ (eq 2).

$$[Fe^{III}(Ph_3PO)_4]^{3+} + HOOH + 2\,^-OH \rightarrow \mathbf{1} \qquad (2)$$

The formation of **1** via the processes outlined in Scheme I appears to be unique and represents a novel route to the formation of a $\mu$-dioxygen bridge by a $L_4Fe(O)/L_4Fe(O)$ coupling reaction. In contrast, formation of a $\mu$-oxo dimer by addition of $Fe^{II}(OPPh_3)_4{}^{2+}$ to **2** does not occur and appears to be precluded by the steric effects of the triphenylphosphine oxide ligands.

**Reactivity of 1.** The binuclear $\mu$-dioxygen complex (**1**) reacts with $^-OH$, pyridine, and other Lewis bases with a stoichiometry of two base molecules per **1**. The reactivity of **1** with HX (X = Cl, Br, I) and $R_4NX$ (X = Br, I) is summarized in Scheme I. Chloride ion in the absence of protons is different from the other halides because it is an inadequate reductant. Instead, addition of $Cl^-$ appears to occur via a sequential process such that a monochloro derivative and a dichloro derivative are formed (see Figure 2).

The dioxygenation by **1** of PhC≡CPh is particularly compelling evidence in support of the $\mu$-dioxygen formulation for **1**.

$$\mathbf{1} + PhC{\equiv}CPh \rightarrow PhC(O)C(O)Ph + 2L_4Fe^{2+} \qquad (3)$$

Although $Ph_3PO$ is not a biological ligand, the halochemistry of Scheme I may be relevant to the myeloperoxidase (MPO, a heme protein) activation of $Cl^-$ and HOOH.[27]

$$Cl^- + HOOH \xrightarrow{MPO} {}^-OCl + H_2O \qquad (4)$$

Some of these intermediates may be similar to the intermediate in the $Fe^{III}Cl_3/H_2O_2/RH$ system in MeCN,[17] which is highly efficient for the epoxidation of olefins and for the chlorination of PhCH(O) to PhC(O)Cl and of cyclohexane to cyclohexyl chloride.

**Acknowledgment.** This work was supported by the National Science Foundation under Grants No. CHE-8212299 and No. CHE-8516247. We are grateful to Prof. Jaan Laane of this department and his graduate student, Vilma Rivera-Gaines, for their assistance with the Raman measurements.

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# Theoretical Study of the Cis–Trans Isomerism in Disubstituted $d^6$ Metal Carbonyls

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*Received April 14, 1988*

The relative stability of the cis and trans isomers of the disubstituted $d^6$ metal carbonyls $M(CO)_4L_2$ (M = Cr, Mo and L = $NH_3$, $PH_3$, $C_2H_4$) and $M(CO)_4LL'$ (M = Mo, L = $C_2H_4$, L′ = $CH_2$) has been studied theoretically through ab initio SCF calculations. Correlation effects were studied for $Cr(CO)_4L_2$ with L = $NH_3$, $PH_3$, $C_2H_4$ through CAS SCF (complete active space SCF) calculations. The results may be summarized as follows: (i) for $M(CO)_4L_2$, with L = $NH_3$, $PH_3$, the cis isomer is more stable than the trans one; (ii) for $M(CO)_4L_2$ with L = $C_2H_4$ or $M(CO)_4LL'$ with L = $C_2H_4$ and L′ = $CH_2$, the trans isomer is more stable than the cis one; (iii) going from Cr to Mo increases the stability of the cis isomer for L = $NH_3$, $PH_3$ but decreases it for L = $C_2H_4$. These theoretical results are in excellent agreement with the bulk of structural data. The results for L = $NH_3$, $PH_3$ are understood easily in terms of competition for $\pi$ back-bonding, but no simple rationale emerges for the greater stability of the trans structure in the case of ethylene or carbene ligands.

## Introduction

Much theoretical work has been devoted to the study of the conformation of organometallics.[1] Comparatively, few theoretical studies deal with the relative stability of geometrical isomers. Noell and Hay studied the structures and relative energies of the cis and trans isomers of $Pt(PH_3)_2XY$ (with X, Y = H, Cl) and of $Pt(CH_3)_2H_2$.[2,3] The $Pt(PH_3)_2H_2$ system was also investigated by Morokuma et al.[4] Dedieu has calculated the relative stabilities of the most probable stereoisomers for the rhodium complexes $RhClL_2$, $H_2RhClL_3$, $H_2RhClL_2$, $H_2RhClL_2(C_2H_4)$, and $H_2RhClL_2(C_2H_5)$.[5] He also investigated the cis–trans conformational isomerism of $H_2Fe(CO)_4$.[6]

For the disubstituted $d^6$ metal carbonyls $M(CO)_4L_2$, two stereoisomers are possible, namely the cis **1** and the trans **2**. For organometallics with a coordination number of 6, the octahedron is usually rather rigid[7] and structures such as **1** and **2** do not interconvert easily (although polytopal rearrangement has been reported in a number of cases[8-14]). For these systems, the question

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