complexes exhibit a well-developed band around 23,000 cm^{-1} (band II) and a broad shoulder centered around 15,800 cm^{-1} (band I). Band I can be safely identified with d–d transitions of the copper(II). In the absence of molar extinction coefficient data, it is difficult to assign band II. It is interesting to note that the electronic spectra of these two complexes are very similar and almost superimposable on each other. One may conclude that if Cu(2-hydroxynaphthaldehyde-2-aminothiophenol) is involved in magnetic exchange, the other complex should also exhibit the same phenomenon. This conclusion has also been supported from the magnetic data.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Oxidation of Bis(π-cyclopentadienyldicarbonyliron) by Anhydrous Ferric Perchlorate in Acetone. A General Route to Complexes of the Types (π-C_5H_5)Fe(CO)$_2$X and (π-C_5H_5)Fe(CO)$_2$L$^+$ [1]

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[(π-C_5H_5)Fe(CO)$_2$]$_2$ is oxidized by 2 mol of Fe(III) in acetonitrile or acetone to give the solvent-bound complexes (π-C_5H_5)Fe(CO)$_2$NCCH$_3^+$ and (π-C_5H_5)Fe(CO)$_2$OC(CH$_3$)$_2^+$. The coordinated acetone in the latter is easily displaced by a variety of ligands giving the complexes (π-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, I, NCS, SCN, ONO$_2$) and (π-C_5H_5)Fe(CO)$_2$L$^+$ (L = py, P(C_6H_5)$_3$, CO, S(C_2H_5)$_2$).

We wish to report details of a simple and general route to complexes of the types (π-C_5H_5)Fe(CO)$_2$X and (π-C_5H_5)Fe(CO)$_2$L$^+$ from bis(π-cyclopentadienyldicarbonyliron).[3] Various methods have previously been used for the preparation of such compounds: (i) Direct reaction of [(π-C_5H_5)Fe(CO)$_2$]$_2$ with halogens gives, for example, (π-C_5H_5)Fe(CO)$_2$I.[4] (ii) Oxidative fission of the metal–metal bond in [(π-C_5H_5)Fe(CO)$_2$]$_2$ by oxygen in the presence of coordinating anions gives, for example, (π-C_5H_5)Fe(CO)$_2$SCN and (π-C_5H_5)Fe(CO)$_2$NCS.[5] (iii) Reduction of [(π-C_5H_5)Fe(CO)$_2$]$_2$ by sodium amalgam, followed by reaction of the anion, without isolation, gives, *e.g.*, (π-C_5H_5)Fe(CO)$_2$S(CH$_3$)$_2^+$.[6] (iv) Isolation of (π-C_5H_5)Fe(CO)$_2$Cl or (π-C_5H_5)Fe(CO)$_2$Br, followed by displacement of the halide ion, gives, *e.g.*, (π-C_5H_5)Fe(CO)$_2$OCOCF$_3$[7] and (π-C_5H_5)Fe(CO)$_2$P(C_6H_5)$_3^+$.[8] In the latter case, (π-C_5H_5)Fe(CO)P(C_6H_5)$_3$Cl is also a product. (v) Isolation of (π-C_5H_5)Fe(CO)$_2$Cl followed by treatment with a neutral ligand in the presence of a halogen acceptor, such as aluminum trichloride, gives, *e.g.*, (π-C_5H_5)Fe(CO)$_2$(NH$_2$NH$_2$)$^+$,[9] (π-C_5H_5)Fe(CO)$_2$NCCH$_3^+$,[10] and (π-C_5H_5)Fe(CO)$_3^+$.[8] (vi) Isolation of (π-C_5H_5)Fe(CO)$_2$Cl, conversion to (π-C_5H_5)Fe(CO)$_3^+$, and treatment with pyridines gives (π-C_5H_5)Fe(CO)$_2$py$^+$,[10] and with azide ion gives (π-C_5H_5)Fe(CO)$_2$NCO.[11] Many of these preparations require anaerobic conditions, anhydrous solvents and atmospheres, extended reaction times, and special apparatus.

Oxidation of metal carbonyl compounds using transition metal oxidants, such as FeCl$_3$ or Ce(IV), often leads to degradation of the complex. For example, *trans,trans,trans*-1-phenyl-6-*p*-tolyl-1,3,5-hexatriene is produced by treatment of the hexatrieneiron tricarbonyl complex with ferric chloride in acetonitrile,[12] and cyclobutadiene is a transient intermediate in the decomposition of cyclobutadieneiron tricarbonyl by ceric ion.[13] However, in other cases simple oxidation products are obtained. Ferric chloride oxidation of Cr(CO)$_5$I$^-$ in acetic acid gives the chromium(I) complex Cr(CO)$_5$I,[14] and the same oxidant converts Co$_6$(CO)$_{15}^{2-}$ into Co$_6$(CO)$_{16}$.[15]

We find that [(π-C_5H_5)Fe(CO)$_2$]$_2$ is rapidly and quantitatively oxidized in a variety of solvents by Fe(III) (either as Fe(ClO$_4$)$_3$ or Fe(OH$_2$)$_6$Cl$_3$). In strongly coordinating solvents, the solvent-bound complex formed in the oxidation is readily isolated; for example, from acetonitrile we isolate (π-C_5H_5)Fe(CO)$_2$NCCH$_3^+$. In the weakly coordinating solvent acetone, the initial product of oxidation is the solvento complex (π-C_5H_5)Fe(CO)$_2$(OC(CH$_3$)$_2$)$^+$. The weakly bound solvent molecule is easily displaced by a variety of neutral and anionic ligands to give the complexes (π-C_5H_5)Fe(CO)$_2$L$^+$ (L = neutral ligand) and (π-C_5H_5)Fe(CO)$_2$X (X = anionic

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ligand). In contrast to the preparations outlined above, this route is completely general and requires no special reaction conditions.

Experimental Section

Bis(π-cyclopentadienyldicarbonyliron) (Alfa Inorganics) was recrystallized from dichloromethane–hexane before use. The anhydrous ferric perchlorate (G.F. Smith) was stored in a glove bag, desiccated with P_4O_{10}. Before use, it was standardized by its spectrophotometric analysis as the tris(1,10-phenanthroline) complex.[16] Six estimations on two samples indicated the ferric perchlorate contained a mean of $10.94 \pm 0.05\%$ ferric ion. Ligands used were all obtained commercially and used without further purification. Acetone (reagent grade) was dried over anhydrous magnesium sulfate. Acetonitrile (commercial grade) was distilled from P_4O_{10} in an atmosphere of nitrogen. Spectrograde acetonitrile was used without purification.

Infrared spectra were measured either in KBr pellets on a Beckman IR12 spectrophotometer or in KBr pellets, Nujol mulls, or dichloromethane solutions on a Perkin-Elmer 421 spectrophotometer. Visible spectra were measured in 1-cm silica cells on a Cary 14 spectrophotometer. Nmr spectra were taken on a Varian A-60 spectrometer in chloroform-d_1 or acetone-d_6 using tetramethylsilane as an internal standard. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

1. **Stoichiometry.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ was treated with an excess of anhydrous ferric perchlorate in acetonitrile. The initial concentrations of iron dimer and ferric perchlorate were 1.01×10^{-3} and 7.85×10^{-3} *M*, respectively. Spectrophotometric analysis of the ferrous ion produced as its tris(phenanthroline) complex[16] gave a final concentration of 2.14×10^{-3} *M* (average of three determinations).

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0.4014 g, 0.00114 mol) in acetonitrile (40 ml) was oxidized with an excess of anhydrous ferric perchlorate (1.6682 g, 0.00328 mol) in acetonitrile (25 ml) under nitrogen in the absence of light for 20 min. After filtration, the solution was chromatographed on Florisil (3 cm × 10 cm column) using acetonitrile as eluent. The yellow eluates were diluted to 100 ml, and 5 ml of the diluted solution was further diluted to 50 ml. The absorbance at 370 nm (ϵ_{max} 735[17]) indicated that $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ was formed in 93% yield.

2. **Detection of the Intermediate in Acetone.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0.55 g) in acetone (20 ml) was treated with anhydrous ferric perchlorate (2.0 g) in acetone (20 ml). The solution was evaporated in a stream of nitrogen, and the black oily material was extracted with dichloromethane (five 20-ml portions). The combined extracts were filtered through a 1 in. × 0.5 in. bed of Florisil and the dichloromethane was evaporated in a stream of nitrogen. *Caution! Complete evaporation of these solutions to dryness may be dangerous. The complex $(\pi\text{-}C_5H_5)Fe(CO)_2OClO_4$ which could form may be explosive.* The nmr spectrum of the solution of the red solid in acetone showed resonances at τ 8.58 (solvent), 8.30 (singlet, coordinated acetone), 5.04 (singlet, π-cyclopentadienyl); the ratio of the latter two peaks was 6:5. The spectrum, therefore, indicates that in acetone the intermediate is $(\pi\text{-}C_5H_5)Fe(CO)_2OC(CH_3)_2^+$.

3. **Preparations.**—*Warning!* Several of the following preparations call for the use of solutions containing both perchlorate ion and labile organometallic complexes. The dangers with regard to the explosion of metal perchlorates have been well documented.[18] In working with such solutions or with solids containing perchlorate due care should be taken.

(a) **$(\pi\text{-}C_5H_5)Fe(CO)_2Cl$.**—The dimer $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.13 g, 0.0032 mol) in acetone (25 ml) was treated with $Fe(H_2O)_6Cl_3$ (1.83 g, 0.0067 mol) in acetone (25 ml) for 1 hr, during which time the brown solution turned burgundy. Sodium chloride (5.12 g, 0.086 mol) in water (50 ml) was added, causing an immediate color change. The acetone was evaporated off, the aqueous solution was extracted with dichloromethane (five 20-ml portions), and the extracts were dried overnight over anhydrous $MgSO_4$. After addition of hexane (50 ml) the dichloromethane was removed on a rotary evaporator. Cold pentane was added and the red crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (0.603 g, 50%) were filtered and dried.

(b) **$(\pi\text{-}C_5H_5)Fe(CO)_2Br$.**—A reaction involving $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.02 g, 0.0029 mol), $Fe(H_2O)_6Cl_3$ (1.91 g, 0.0071 mol), and sodium bromide (5.45 g, 0.0053 mol) yielded $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ (0.700 g, 48.5%) by the method described in (a).

(c) **$(\pi\text{-}C_5H_5)Fe(CO)_2ONO_2$.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.00 g, 0.0028 mol) was treated with anhydrous ferric perchlorate (2.80 g, 0.0055 mol) in acetone (50 ml) (addition of a few drops of reaction solution to about 20 ml of water after *ca.* 5 min gave a clear solution indicating complete consumption of the dimer). Addition of sodium nitrate (5.87 g, 0.0068 mol) and working up as described before yielded $(\pi\text{-}C_5H_5)Fe(CO)_2ONO_2$ (0.293 g, 22%).

(d) **$(\pi\text{-}C_5H_5)Fe(CO)_2NCS$.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.02 g, 0.0029 mol) was oxidized by anhydrous ferric perchlorate (3.01 g, 0.0059 mol) in acetone (50 ml); NH_4SCN (10.35 g, 0.13 mol) in water was added, and the acetone was removed by evaporation. The aqueous solution was extracted with dichloromethane (5 × 20 ml) and the extracts were dried overnight over magnesium sulfate. The dichloromethane solutions containing both linkage isomers were evaporated to *ca.* 5 ml and chromatographed on a Florisil column (3 cm × 30 cm) using dichloromethane as the eluent. The yellow band was collected and reduced in volume to *ca.* 5 ml, and pentane (50 ml) was added. Yellow crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2NCS$ were collected.

(e) **$(\pi\text{-}C_5H_5)Fe(CO)_2SCN$.**—The red band from the chromatography in (d) was removed with acetone, the acetone was evaporated, and the residue was dissolved in $(C_2H_5)_2O$ (50 ml). After evaporation to 10 ml in a stream of nitrogen, pentane (50 ml) precipitated red crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2SCN$.

(f) **$(\pi\text{-}C_5H_5)Fe(CO)_2I$.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.01 g, 0.0029 mol) was dissolved in nitrogen-saturated acetone and mixed with $Fe(ClO_4)_3$ (3.75 g, 0.0074 mol) in the same solvent in a nitrogen atmosphere. Tetra-*n*-butylammonium iodide (5.00 g, 0.014 mol) in acetone was added and the resulting solution was evaporated to dryness. Dichloromethane (100 ml) was added along with hexane (100 ml) and the solvent was evaporated to a small volume. Addition of cold pentane deposited dark purple crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ (0.878 g, 51.2%).

(g) **$[(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3]PF_6$.**—The solutions obtained in the stoichiometry determinations were evaporated and a large excess of NH_4PF_6 in water was added. Further evaporation deposited crystals of $[(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3]PF_6$.

(h) **$[(\pi\text{-}C_5H_5)Fe(CO)_2py]B(C_6H_5)_4$.**—$[(\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.50 g, 0.0014 mol) and anhydrous $Fe(ClO_4)_3$ (1.58 g, 0.0031 mol) were dissolved in acetone, mixed, and stirred for a further 15 min. The acetone was evaporated, aqueous NH_4PF_6 was added, and the yellow crystals formed were removed by filtration. They were converted into the tetraphenylborate salt by dissolution in water and addition of aqueous $NaB(C_6H_5)_4$. Yellow crystals of $[(\pi\text{-}C_5H_5)Fe(CO)_2py]B(C_6H_5)_4$ (0.493 g, 30.0%) resulted.

(i) **$[(\pi\text{-}C_5H_5)Fe(CO)_2P(C_6H_5)_3]ClO_4$.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.00 g, 0.0028 mol) and $Fe(ClO_4)_3$ (3.23 g, 0.0063 mol) were dissolved in acetone and mixed. Triphenylphosphine (2.6 g, 0.01 mol) was added and the solution was stirred for 45 min. The solution was evaporated to *ca.* 5 ml and chromatographed on Florisil (3 cm × 30 cm column) using acetone as the eluent. The yellow band was collected, and addition of water caused precipitation of yellow crystals of $[(\pi\text{-}C_5H_5)Fe(CO)_2P(C_6H_5)_3]ClO_4$ (0.700 g, 22.3%).

(j) **$[(\pi\text{-}C_5H_5)Fe(CO)_2S(C_2H_5)_2]PF_6$.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1.00 g, 0.0028 mol) and $Fe(ClO_4)_3$ (4.21 g, 0.0083 mol) were dissolved in acetone and mixed, and after 5 min the solution was run through a Florisil column (3 cm × 30 cm) using acetone as eluent. To the bright red eluted solution were added NH_4PF_6 (6.5 g) and diethyl sulfide (16 ml, 0.15 mol) and the mixture was stirred for 30 min. Chromatography on Florisil (3 cm × 30 cm column) using acetone as eluent, addition of aqueous ammonium hexafluorophosphate (5 g in 100 ml) to the orange-red eluate, and evaporation of the organic solvent resulted in yellow $[(\pi\text{-}C_5H_5)Fe(CO)_2S(C_2H_5)_2]PF_6$ (1.0 g, 4.32%).

(k) **$[(\pi\text{-}C_5H_5)Fe(CO)_3]B(C_6H_5)_4$.**—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0.50 g, 0.0014 mol) was oxidized with anhydrous $Fe(ClO_4)_3$ (1.50 g, 0.0030 mol) in acetone (oxygen free, 60 ml). After 25 min, the solution was filtered, concentrated, and chromatographed on Florisil (3 cm × 20 cm column) using oxygen-free acetone as eluent. The red eluates were evaporated to *ca.* 50 ml and carbon monoxide was bubbled through for 30 min at atmospheric pressure. The solution was evaporated to dryness, and the solid was extracted with benzene to remove the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ produced by reduction of the acetone complex on the column. The yellow crystals were extracted with acetone and excess sodium

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TABLE I

No.	Compd	% C Calcd	% C Found	% H Calcd	% H Found	% halogen Calcd	% halogen Found	% N Calcd	% N Found	% other Calcd	% other Found
1	(π-C_5H_5)Fe$(CO)_2$Cl	39.58	39.81	2.37	2.38	16.69	16.94				
2	(π-C_5H_5)Fe$(CO)_2$Br	32.73	32.60	1.96	1.82	31.11	31.30				
3	(π-C_5H_5)Fe$(CO)_2$I	27.65	27.84	1.63	1.53	41.78	41.90				
4	(π-C_5H_5)Fe$(CO)_2ONO_2$	35.15	34.97	2.09	2.06	5.86	5.75				
5	(π-C_5H_5)Fe$(CO)_2$NCS	40.85	41.02	2.13	2.13			5.96	5.98	13.62 (S)	13.46 (S)
6	(π-C_5H_5)Fe$(CO)_2$SCN	40.85	40.97	2.13	2.04			5.96	5.95	13.62 (S)	13.40 (S)
7	[(π-C_5H_5)Fe$(CO)_2NCCH_3$]PF_6	29.75	29.43	2.21	2.35			3.86	3.61		
8	[(π-C_5H_5)Fe$(CO)_2$py]B$(C_6H_5)_4$	75.92	77.90	5.27	5.42			2.46	2.73		
9	[(π-C_5H_5)Fe$(CO)_2$P$(C_6H_5)_3$]ClO_4	55.81	56.18	3.72	3.54					5.76 (P)	4.91 (P)
10	[(π-C_5H_5)Fe$(CO)_2$S$(C_2H_5)_2$]PF_6	32.04	32.23	3.64	3.73					7.77 (S)	7.64 (S)
11	[(π-C_5H_5)Fe$(CO)_3$]B$(C_6H_5)_4$	73.32	73.33	4.81	4.77						

tetraphenylborate (2 g) in acetone was added. Water (15 ml) was added and the acetone was removed by evaporation. Yellow crystals of [(π-C_5H_5)Fe$(CO)_3$]B$(C_6H_5)_4$ (0.40 g, 25%) were deposited.

Results

Analytical data for the complexes prepared are given in Table I. They were also characterized by comparing their CO stretching frequencies with the known values (compounds 1, 2, 3, and 5, from ref 5; compounds 7, 8, 9, and 11, from ref 10). Two new compounds were also prepared, (π-C_5H_5)Fe$(CO)_2ONO_2$ and [(π-C_5H_5)Fe$(CO)_2$S$(C_2H_5)_2$](PF_6), and their ν_{CO} bands are at 2060 (s), 2007 (s) and 2063 (s), 2018 cm^{-1} (s), respectively, in KBr pellets.

The pmr spectrum of the diethyl sulfide complex in acetone d_6 shows resonances at τ 4.83 (singlet, π-cyclopentadienyl), 7.60 (quartet), and 9.18 (triplet) *vs.* TMS. The quartet–triplet pattern and the integrated peak ratios are consistent with a coordinated diethyl sulfide group.

The attempted preparations of bisulfite and nitrite complexes were unsuccessful, uncharacterized products being obtained. The addition of either ammonium acetate in acetone or sodium fluoride in methanol to solutions of the intermediate acetone complex gave only the starting material [(π-C_5H_5)Fe$(CO)_2]_2$.

The preparations described in the Experimental Section were carried out in acetone. In a few cases duplicate experiments were carried out using methanol as the solvent. The results were equally successful, and although the methanol complex (π-C_5H_5)Fe$(CO)_2$-$HOCH_3^+$ has not been characterized, the reactions in methanol are probably analogous to those in acetone. Attempts were also made to use the acetonitrile complex (π-C_5H_5)Fe$(CO)_2NCCH_3^+$ as a reaction intermediate. In an acetonitrile solution 0.1 *M* in tetra-*n*-butylammonium bromide and 10^{-3} *M* in complex, no anation was observed after 1–2 hr. Outer-sphere bromide ion ion pairing was observed spectrophotometrically.

Discussion

One mole of bis(π-cyclopentadienyldicarbonyliron) reacts with excess anhydrous ferric perchlorate in acetonitrile, according to the reaction

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2Fe^{3+} \longrightarrow 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+ + 2Fe^{2+}$$

The acetonitrile complex can be isolated as its hexafluorophosphate salt as described in the Experimental Section. Acetonitrile is strongly bound and is not easily displaced by other ligands.

If the oxidation is carried out in acetone or methanol, however, the weakly bound solvent molecule in (π-C_5H_5)Fe$(CO)_2S^+$ (S = solvent) is easily displaced by a variety of ligands to give the complexes (π-C_5H_5)Fe$(CO)_2$X (X = Cl, Br, I, ONO_2, NCS, SCN) and (π-C_5H_5)Fe$(CO)_2L^+$ (L = py, P$(C_6H_5)_3$, S$(C_2H_5)_2$, CO). The coordinated acetone in (π-C_5H_5)Fe$(CO)_2$OC$(CH_3)_2^+$ has been observed by nmr as described in the Experimental Section. The preparations are direct and simple, and the yields are generally good although no attempt was made to maximize them. Especially striking are the direct preparations of (π-C_5H_5)Fe$(CO)_3^+$ and (π-C_5H_5)Fe$(CO)_2$S$(C_2H_5)_2^+$; the tricarbonyl complex was prepared previously by a lengthy high-pressure reaction,[8] and the complex (π-C_5H_5)Fe$(CO)_2$S$(CH_3)_2^+$, analogous to the diethyl sulfide complex, by an involved route *via* (π-C_5H_5)Fe$(CO)_2^-$, which requires rigorously anaerobic and anhydrous conditions.[6]

The synthetic route described here is general for complexes of the types (π-C_5H_5)Fe$(CO)_2$X and (π-C_5H_5)Fe$(CO)_2L^+$ but is limited to ligands which do not react with the solvent, are capable of displacing the coordinated solvent molecule, and form stable complexes when bound to (π-C_5H_5)Fe$(CO)_2^+$. We are currently extending the reaction to more complicated ligand systems and are investigating in detail the properties and labilities of a series of solvento complexes of the type (π-C_5H_5)Fe$(CO)_2S^+$.

The metal–metal bond in [(π-C_5H_5)Fe$(CO)_2]_2$ has been oxidized in acetone and acetonitrile at carbon and platinum electrodes.[17] The electrochemical reactions are also useful for preparing (π-C_5H_5)Fe$(CO)_2$X and (π-C_5H_5)Fe$(CO)_2L^+$ type complexes.

[Ru$(bipy)_2Cl_2$](PF_6), [(π-$C_5H_5)_2$Fe](BF_4), and other Fe(III) salts also oxidize the metal–metal bond.[19] However, because of solubility difficulties, in order to avoid the introduction of potentially coordinating anions, and for a variety of other reasons, Fe$(ClO_4)_3$ is by far the most useful oxidant that we have found.

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