Synthesis, Reactivity, and Catalytic Behavior of Iron/Zinc-Containing Species Involved in Oxidation of Hydrocarbons under Gif-Type Conditions

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Abstract: The present study explores the nature and reactivity of iron- and zinc-containing species generated in hydrocarbon-oxidizing Gif IV-type solutions (Fe catalyst/Zn/O2 in pyridine/acetic acid (10:1 v/v)). The ultimate goal of this investigation is to unravel the role of metal sites in mediating dioxygen-dependent C–H activation, which in the case of Gif chemistry demonstrates an enhanced reactivity for the ketonization of secondary carbons. Reaction of [Fe3O(O2CCH3)6(py)3] (1) with zinc powder in CH3CN/CH3COOH or CH3Cl/CH3COOH affords the trinuclear compound [Zn2FeIII(O2CCH3)6(py)2] (2). Single-crystal X-ray analysis confirms that one monodentate and two bidentate acetate groups bridge adjacent pairs of metals with the iron atom occupying a centrosymmetric position. The analogous reduction of 1 in py/CH3COOH (10:1, 5:1, 2:1 v/v) yields [FeII(O2CCH3)2(py)4] (3), [FeII(O2CCH3)3(py)3] (4), and [Zn(O2CCH3)2(py)2] (5) depending on the isolation procedure employed. Compound 3 possesses a distorted octahedral geometry, featuring a C2 axis bisecting the equatorial, pyridine-occupied plane, whereas the two acetate groups reside along the perpendicular axis. Compound 4 is a one-dimensional solid constructed by asymmetric disordered units. Two bidentate and one monodentate acetate bridges connect the two iron sites, with the monodentate bridge also acting as a chelator to one ferrous center. The two iron centers exhibit weak antiferromagnetic coupling. Compounds 3 and 4 are also accessible from the reduction of 1 with iron powder or treatment with H2/Pd. Solutions of 3 and 4 in pyridine or py/CH3COOH react with pure dioxygen or air to eventually regenerate 1 in a concentration-dependent manner. Oxidation of 2 in py/CH3COOH with pure dioxygen or air yields [FeII2Zn0.78(2)O(O2CCH3)6{(py)3}2(py)1]′ (1′) and [Zn2O2CCH3(py)2] (6). Compound 1′ is isostructural to 1, exhibiting rhombohedral symmetry at 223 K. The filtrate of the reduction of 1 with zinc in neat pyridine, when exposed to dioxygen, affords dichroic red–green crystals of monoclinic [FeII2ZnO(O2CCH3)6(py)3]′′ (1″). Species 1″ yields products identical with those provided by 1 under reducing conditions. Compounds 2–6 are related by pyridine-dependent equilibria, as demonstrated by mutual interconversions and electronic absorption data in pyridine and py/CH3COOH solutions. In non-pyridine solutions, Zn-containing species 5 and 6 rearrange to the crystallographically characterized species [Zn(O2CCH3)2(py)3] (7) and [Zn2O(O2CCH3)6(py)2] (8). Compound 7 is a one-dimensional solid featuring a chain of Zn sites linked by a bidentate acetate group while additionally coordinated by a chelating acetate. Compound 8 is isostructural to 2. Further perturbations of the described structures are apparent in iron-containing species, such as the pseudo-seven-coordinate iron in [PPh3]2+[FeIII(O2CCH3)3(py)] (9), which is obtained from the reaction of 3 with [PPN][O2CCH3], and the water-coordinated iron in [FeIII(H2O)4(trans-py)]2[O2CCH3]2 (10), which reveals an extensive two-dimensional network of hydrogen-bonding interactions. The pyridine-free species [FeII(O2CCH3)3(OS)(CD3)]2 (11) is isolable upon extensive incubation of 3 in (CD3)2SO. Compound 11 exhibits a remarkable one-dimensional structure, featuring four different types of acetate groups. Catalytic oxidations of adamantane, isopentane, benzene, toluene, cis-stilbene, and pyridine mediated by the system 1 (or 2–4)/Zn/O2 in py/AcOH (10:1) afford product profiles which are not fully compatible with the reported outcome of analogous oxidations by hydroxyl radicals or biologically relevant high-valent iron–oxo species alone. The intermolecular deuterium kinetic isotope effect for the oxidation of adamantane to adamantaneone is small (kD/kH = 2.01(12)) by comparison to values obtained for oxidation of hydrocarbons by biological oxygenses. Employment of hydrogen peroxide, t-BuOOH, or peracetic acid as potential oxo donors does not provide viable shunt pathways in the catalytic oxygenation of adamantane. The nature of active oxidant in Gif IV-type oxidation is discussed in light of these structural and functional findings.

Introduction

A substantial number of non-heme, iron-containing biological sites1 have recently emerged as required or circumstantial centers in dioxygen transport and activation. Both mononuclear2 and dinuclear3 iron centers have been firmly recognized to reside in a protein cavity in which a putative ferric (alkyl/hydro)peroxo and/or a high-valent iron–oxo intermediate is generated upon dioxygen activation. Of particular interest in this context is the currently emerging4 dinuclear FeIIIIV–(μ-O)–FeIV core and its precursor FeII(μ-O)–FeIII mienity that may prove to be as versatile active oxidants in non-heme iron systems as the

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putative Fe$^{IV}$-Oresidue unit has been in heme iron chemistry. In principle, potent oxidants of this kind can execute substrate oxygenation/desaturation or generate a biologically beneficial (and occasionally detrimental) long-lived radical upon interaction with biological material. Reactive oxygen species (superoxide, singlet oxygen, alkoxyl/hydroxyl radicals, nitric oxide) have also been implicated in degenerative biological oxidations via mechanisms involving, 

One inspirational example of hydroxylating activity is the remarkable oxidation of methane to methanol mediated by the well-documented diiron site of the hemeoylase component of soluble methane monooxygenase (sMMO). The crystal structures have revealed the presence of a hydroxo-bridged diiron center in H$_{ox}$ (Fe$^{IV}$=Fe$^{III}$) and a hydroxo-devidi iron center in H$_{red}$ (Fe$^{IV}$=Fe$^{II}$). The lack of hydroxide bridge in H$_{ox}$ is coordinately compensated by a unique carboxylate shift (Glu 243) from a terminal (H$_{ox}$) to a monodentate-bridging (H$_{red}$) diiron site of Methanolococcus capsulatus (Figure 1), as well as the recent structure (2.0 Å) of the H$_{ox}$ protein from Methylosinus trichosporum OB3b, which assumes a nearly terminal position, with a buffer-derived bidentate acetate occupying this position in the 2.2 Å resolution structure.

The remarkable oxidation of methane to methanol mediated by the iron (or copper) ions.

although only a handful of these systems employ dioxygen, the category includes hydrocarbon-oxygenizing systems such as [Fe$_2$O(TPA)(H$_2$O)$_3$]$_{18}$-tBuOOH(H$_2$O)$_2$, [Fe$_2$O(L$_2$)$_2$]/tBuOOH$_2$, [Fe$_2$O(OAc)$_2$(bipy)$_2$]/Cl$_2$:tBuOOH$_2$O$_2$, [Fe$_2$O(OAc)$_2$(tiim)$_2$]$_{16}$-H$_2$O, [Fe$_2$O(OAc)$_2$(tiim)$_2$]$_{16}$-H$_2$O$^-$, [Fe$_2$O(HB(pz)$_3$)$_2$(X)$_2$]/ZnO$_2$ (X = OAc, hfacac), and [Fe$_2$O(salen)$_2$]/2-mercaptoethanol/O$_2$. Although only a handful of these systems employ dioxygen, some of those featuring alternative oxo donors have been established to operate via a dioxygen-dependent pathway.

Concomitantly, the terminal water molecule in H$_{ox}$ is almost dissociated in H$_{red}$. These atomic translocations upon reduction lead to a core structure that is nearly five-coordinate at the iron site, although the semisemicoordinated positions are at orthogonal orientations.

Synthetic analogues of dinuclear iron sites have been instrumental in elucidating structural aspects pertaining to the enzymatic center of sMMO, but instances of functional behavior are scarce. The latter category includes hydrocarbon-oxygenizing systems such as [Fe$_2$O(TPA)(H$_2$O)$_3$]$_{18}$-tBuOOH(H$_2$O)$_2$, [Fe$_2$O(L$_2$)$_2$]/tBuOOH$_2$, [Fe$_2$O(OAc)$_2$(bipy)$_2$]/Cl$_2$:tBuOOH$_2$O$_2$, [Fe$_2$O(OAc)$_2$(tiim)$_2$]$_{16}$-H$_2$O, [Fe$_2$O(OAc)$_2$(tiim)$_2$]$_{16}$-H$_2$O$^-$, [Fe$_2$O(HB(pz)$_3$)$_2$(X)$_2$]/ZnO$_2$ (X = OAc, hfacac), and [Fe$_2$O(salen)$_2$]/2-mercaptoethanol/O$_2$. Although only a handful of these systems employ dioxygen, some of those featuring alternative oxo donors have been established to operate via a dioxygen-dependent pathway.


(14) Abbreviations used: TPA, tris-(2-pyridylmethyl)amine; tmn, tris-(1-imidazolylmethyl)-2-phenylethylamine; HB(pz), hydrotris(3,5-dimethylpyrazolyl)borate; hfacac, hexafluoroacetyacetone; salen,N′,N′-bis(salicylidene)ethylenediamine; EDTA, ethylenediamine-N,N′,N′,N′-tetraacetate; TAT, attenuated total internal reflectance; PBN, bis(triphenylphosphine)iminium; Me-TACN, 1,4,7-trimethyl-1,4,7-triazacyclononane; ICP, inductively coupled plasma; PrO$_5$, bis[2-(41-methylphenoxyl-1,3-oxazolinyl)]methane; PheMe$_3$Eda, N,N,N′-trimethyl-1,4,4-dimethyl-3-(4-tert-butyl-4-hydroxyphenyl)butyl]ethylenediamine; BPhMe, bis(1-methyl-2-imidazolylphenyloxy) methane; BPhOH, bis(1-[(2-imidazolylphenyloxy) methylene]benzene; BID$_2$EHA, 1,1-bis(1-methyl-2-imidazolyl)-1-(3,3-dimethyl-4-hydroxyphenyl)ethane; CusMe$_3$Eda, 1,3-phenyl-1-oxacycloheptatriene; PAH, picolinic acid; T.


However, the nature of the active oxidant(s) involved has remained largely unspecified or is a matter of debate.

On the other hand, iron species that have received less attention as structurally competent mimics have nonetheless been long implicated in the celebrated hydrocarbon-oxidizing systems, such as the century-old Fenton reagent (FeIII/H2O2, aqueous (pH 2)) and the more biologically relevant, dioxygen-dependent Udenfriend (FeIII/EDTA/ascorbate/O2)31 and GifII2 systems. Gif chemistry has achieved notoriety owing to its superior product yield and selectivity as well as its potential biomimetic value. The catalysts involved in Gif solutions operate primarily in providing the catalytic entity (electrochemical cathode) or the equivalent FeIII/H2O2 and FeIII/δ-BuOOH (60 °C) combinations. Additives such as picolinic acid (PAH) can substantially enhance the rate of the reaction.24 Typical reagents employing PAH include combinations such as FeCl3/PAH/H2O2 (1:4:4) in pyridine or py/acOH (10:1) and FeIII(PA)/H2O2 (1:20) in py/acOH (2:1). Copper-based Gif catalysts have also been reported.

The proposed mechanistic pathways purported to account for the suggested selectivity of Gif systems vis-à-vis hydrocarbon substrates (sec > tert > prim) deviate from current mechanistic considerations as applied to P-45026 or sMMO27 biological oxidations. These mechanisms further reflect the continuing debate concerning as applied to P-4505,26 or sMMO4,27 biological oxidations. The original Barton mechanism,22 pertaining to the homoalkylation of cyclohexanol. The involvement of hydroxyalkyl radicals in metal-mediated oxidations by alkoxyl radicals has been postulated as being the active oxidant, generated by FeII, dependent decomposition of t-BuOOH. The required Minisci steps (eqs 7–15) predict a ketene:alcohol ratio of ≥1. Product selectivity may be influenced by the solvent-dependent competitive rates of eqs 9–10. Corroborative evidence for the operation of the radical mechanism has been provided by Ingold and coworkers28 for Gif-type chemistry involving a variety of alkylhydroperoxides. These and related studies31 have been instrumental in demonstrating the ubiquitous nature of alkyl and alkylperoxy radicals in metal-mediated oxidations by t-BuOOH.34 Analogous interpretations38,39 pertaining to catalytic oxidations mediated by P-450-type mimics coupled to alkylhydroperoxides have been similarly cautious in regards to the

\[
\begin{align*}
\text{Fe}^{III} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{IV} + \text{H}_2\text{O} + \text{H}_2\text{O} \\
\text{Fe}^{IV} = \text{O} + \text{c-C}_6\text{H}_5 & \rightarrow \text{Fe}^{IV} (\text{OH}) (\text{c-C}_6\text{H}_5) \\
\text{Fe}^{IV} (\text{OH})(\text{c-C}_6\text{H}_5) & \rightarrow \text{Fe}^{III} (\text{OH})(\text{OO-c-C}_6\text{H}_11) \\
\text{Fe}^{III} (\text{OH})(\text{OO-c-C}_6\text{H}_11) & \rightarrow \text{Fe}^{II} + 2\text{OH}^- + \text{c-C}_6\text{H}_10(\text{O}) \\
\text{Fe}^{III} (\text{OH})(\text{OO-c-C}_6\text{H}_11) & + \text{reducing agents} \rightarrow \text{c-C}_6\text{H}_11(\text{OH}) \\
\end{align*}
\]

More recent interpretations29 of the FeCl3/PAH/H2O2 system, favor generation of a diferrous FeII-(μ-O2)−FeIII unit that is subsequently converted to the oxenoid FeIII-(μ-O2)−FeIV=O moiety by reaction with 1 equiv of H2O2. Alternative active oxidants such as [FeOOH](PA)(pyH+)] have been proposed30 by virtue of product-profile similarities observed between “oxygenated Fenton” (FeIII(PA)/H2O2 (1:20) in py/acOH (2:1)) and Gif systems, and corresponding discrepancies found between these metal-based systems and genuine hydroxyl radical oxidations.20b However, none of the alleged intermediates have been rigorously detected.

In contrast, the more traditional radical version of this mechanism has been proposed by Minisci31 to account for Gif chemistry employing t-BuOOH. Alkoxyl radicals have been postulated as being the active oxidant, generated by FeII, dependent decomposition of t-BuOOH. The required Minisci steps (eqs 7–15) predict a ketene:alcohol ratio of ≥1. Product selectivity may be influenced by the solvent-dependent competitive rates of eqs 9–10. Corroborative evidence for the operation of the radical mechanism has been provided by Ingold and coworkers28 for Gif-type chemistry involving a variety of alkylhydroperoxides. These and related studies31 have been instrumental in demonstrating the ubiquitous nature of alkyl and alkylperoxy radicals in metal-mediated oxidations by t-BuOOH. Analogous interpretations38,39 pertaining to catalytic oxidations mediated by P-450-type mimics coupled to alkylhydroperoxides have been similarly cautious in regards to the
active oxidant involved.

\[
\text{Fe}^{II} + t\text{-BuOOH} \rightarrow \text{Fe}^{III} + \text{OH}^- + t\text{-BuO}^* \quad (7)
\]

\[
\text{Fe}^{III} + t\text{-BuOOH} \rightarrow \text{Fe}^{II} + \text{H}^+ + t\text{-BuOO}^* \quad (8)
\]

\[
t\text{-BuO}^* + c\text{-C}_6\text{H}_{11} \rightarrow t\text{-BuOH} + c\text{-C}_6\text{H}_{11}^* \quad (9)
\]

\[
t\text{-BuO}^* + t\text{-BuOOH} \rightarrow t\text{-BuOH} + t\text{-BuOO}^* \quad (10)
\]

\[
2t\text{-BuOO}^- \rightarrow 2t\text{-BuO}^* + O_2 \quad (11)
\]

\[
c\text{-C}_6\text{H}_{11}^* + O_2 \rightarrow c\text{-C}_6\text{H}_{11}\text{OO}^* \quad (12)
\]

\[
2c\text{-C}_6\text{H}_{11}\text{OO}^- \rightarrow c\text{-C}_6\text{H}_{11}\text{OOOO}^- c\text{-C}_6\text{H}_{11} \rightarrow
\]

\[
c\text{-C}_6\text{H}_{11}(O) + c\text{-C}_6\text{H}_{11}\text{OH} + O_2 \quad (13)
\]

\[
c\text{-C}_6\text{H}_{11}\text{OO}^- + t\text{-BuOO}^- \rightarrow c\text{-C}_6\text{H}_{11}\text{OOOO}^- t\text{-Bu} \rightarrow
\]

\[
c\text{-C}_6\text{H}_{11}(O) + t\text{-BuOH} + O_2 \quad (14)
\]

\[
c\text{-C}_6\text{H}_{11}^* + t\text{-BuOO}^* \rightarrow c\text{-C}_6\text{H}_{11}\text{OO}^* t\text{-Bu} \quad (15)
\]

Alternative metal-based active oxidants, that have been suggested by Barton29 to form alkyl radicals, include the couple Fe^{II–III}OH/Fe^{IV–V}=O, generated by the competitive Fe^{II}H_{2}O_{2} combination under dioxygen-deficient conditions. The alkyl radical is proposed to be the product of homolytic cleavage within an HO–Fe^{IV–V}–R unit.

The relationship between Gif chemistry and sMMO activity relies on potential structural similarities due to the choice of solvents (py/AcOH) in Gif catalysis and the nature of amino acid residues of the dirion site in sMMO. However, functional analogies are much more tentative and need to be carefully examined. Despite the fact that the peculiar Gif-type selectivity parallels the one encountered in the activity of sMMO for a limited number of substrates,36,37 the following discrepancies exist: (i) Gif catalysts mediate mostly ketonization of secondary carbons38 while sMMO features hydroxylation of primary carbons39; (ii) oxidation of olefins leads largely to ketonization in Gif chemistry,40 as opposed to mostly stereospecific epoxidation by sMMO37 and P-450 systems; (iii) radical-clock experiments indicate41 the presence of diffusely free (long-lived) alkyl radicals in r-tBuOOH/H_{2}O_{2}-based Gif chemistry, but only short-lived (<100 fs) substrate radicals under P-450 activated or sMMO27 oxidations, although results obtained27a,41 with sMMO from *M. trichosporium* suggest longer life spans for the generated alkyl radicals; and (iv) deuterium primary kinetic isotope effect (KIE) values tend to be low (∼2.5)42 in Gif-type oxidations by comparison to intrinsic KIE values for hydroxylations catalyzed by P-450 isoymes/mimics (KIE = 10–14;43 more modest and disperse values have also been measured44) and sMMO27a (KIE values larger than 50 have been reported44 for methane with *M. trichosporium*, although ethane exhibits a value of 4).

To gain a more intimate view of the role of metal sites in Gif-type chemistry as well as explore possible connectivities with structural/functional aspects pertaining to sMMO, we have turned our attention to Gif-type systems (Fe^{III/II}/O_{2}/I/z/substrate in py/AcOH) with emphasis on the basic iron acetic [Fe_{2}O(O_{2}CCH_{3})_{6}py] {2+} system (I) as starting material and catalyst. Several lines of evidence make the choice of this mixed-valent species attractive: (i) the metal ligation (Fe=O = 1.9 Å, Fe⋯Fe = 3.4 Å)45 is representative of corresponding moieties and metrical parameters in sMMO;6a(ii) the ferrous site in I can be readily replaced by a non-redox ion such as Mg^{2+} or Zn^{2+}, practically reducing the species to a dinuclear iron compound; (iii) compound I has been isolated46 from catalytic mixtures and successfully used47 as a source of iron in Gif-type oxidation of hydrocarbons (Gif IV); and (iv) the all-ferric [Fe_{2}O(O_{2}CCH_{3})_6 (py)_{3}] {3+} is reported48 to mediate epoxidation of olefins by molecular oxygen.

The following are pertinent questions that need to be progressively addressed in this study: (i) What are the characteristics of the reduced iron sites that may be accountable for dioxygen binding and activation during catalytic turnovers? (ii) What are the products of autoxidation of these reduced species upon exposure to dioxygen? (iii) Are there any discernible structural similarities that may allow us to draw legitimate analogies between iron centers present in Gif-type solutions and at the active site of sMMO? (iv) How does the product profile of substrate oxidations mediated by the I/z/ O_{2} system, and variations thereof, compare in terms of yield, regio(chemo)specificity, and KIE values to other Fenton- and Gif-type systems as well as to sMMO and P-450 hydroxylase activity? (v) Is there any evidence that the isolable “catalysts” are kinetically competent to mediate substrate oxidation and can intermediates of dioxygen activation be detected and related to substrate turnover?

Answers to questions i–iv are investigated in this article. Question v needs to be addressed on the basis of the results of a comprehensive kinetic study coupled with a systematic search for the detection of intermediates. Such work is currently in
progress and will be reported in due course. Aspects of the present study have been published in a preliminary report.\(^4^9\)

**Experimental Section**

**Preparation of Compounds.** All operations were performed under a pure dinitrogen or argon atmosphere using Schlenk techniques on an inert gas/vacuum manifold or in a drybox (O\(_2\), H\(_2\)O < 1 ppm). Hexane, petroleum ether, and toluene were distilled over Na, and THF and diethyl ether over Na\(_2\)HPO\(_4\). Acetonitrile and methylene chloride were distilled under CaH\(_2\). Ethanol and methanol were distilled over the corresponding magnesium alkoxide, and acetone over drierite. Anhydrous pyridine and dimethyl sulfoxide (water < 0.005%) and double-distilled acetic acid (metallic impurities in ppm) were purchased from Aldrich. All solvents, with the exception of methanol, were degassed by three freeze–pump–thaw cycles. Methanol and water were degassed by bubbling nitrogen or argon for 0.5 h. Compounds [Fe\(_3\)O(O\(_2\)CCH\(_3\))\(_6\)](py)\(_3\) (1)\(^1\) and [Fe\(_2\)ZnO(O\(_2\)CCH\(_3\))\(_6\)](py)\(_3\) (3)\(^1\) were prepared according to literature procedures. Other starting materials were purchased from Aldrich and are of the highest available purities.

\([\text{ZnFe}\(_{1}\)(O\(_2\)CCH\(_3\))]\(_6\)(py)\(_2\)\) (2). Zn powder (1.32 g, 0.02 mol) was added to a brown-black solution of [Fe\(_3\)O(O\(_2\)CCH\(_3\))\(_6\)](py)\(_3\) (1) (342 mg, 0.40 mmol) in 4.5 mL of acetonitrile and 0.45 mL of acetic acid. The reaction mixture was stirred for 0.5 h, and the excess Zn was filtered off. The light yellow supernatant afforded the pure product 2 (630 mg, 75% based on Fe) as light-yellow plates upon cooling (−20 °C).

The same product can be obtained pure from the following reaction solvents: acetonitrile (3.0 mL)/acetic acid (1.5 mL); dichloromethane (4.5 mL)/acetic acid (0.45 mL); and pyridine (3.0 mL)/acetic acid (1.5 mL). In the last case, the pure product was obtained by slow diffusion of diethyl ether into the yellow-green supernatant at −20 °C (vide infra for an alternative method of preparation).

\[\text{Fe}\(_3\)O(O\(_2\)CCH\(_3\))\(_6\)](py)\(_3\) (1) (342 mg, 1.0 mmol) in 10 mL of pyridine and 5 mL of acetonitrile was added to the yellow-green filtrate afforded the pure product as yellow-green precipitate. The latter retains Fe(III) according to the Moessbauer data. Preactivation of the Zn dust (washing with dilute HCl) was essential, for the product is exceedingly air-sensitive. Compound 4 was also obtained pure, but in a feathery form, from pyridine (4.0 mL)/acetic acid (0.8 mL) by diffusion of diethyl ether at 10 °C or from pyridine (3.0 mL)/acetic acid (1.5 mL) followed by diffusion of diethyl ether at −20 °C. \(^{19}\)Fe NMR ([CD\(_3\)]\(_2\)SO): 1.21 M): \(\delta_{\text{H}} 1.02 \text{ mm/s} (\Delta E_0 = 2.74 \text{ mm/s, } \Gamma = 30 \text{ mm/s). Anal. Calcld for C\(_{14}\)H\(_{22}\)N\(_2\)Fe(CO\(_2\)), C, 37.32; H, 3.98; N, 3.95. Found: C, 37.32; H, 4.13; N, 3.89.}

**[Zn(O\(_2\)CCH\(_3\))]\(_2\)(py)\(_2\) (5).** Diethyl ether was slowly diffused to a solution of [Zn\(_2\)(O\(_2\)CCH\(_3\))]\(_2\)-2H\(_2\)O (439 mg, 2.0 mmol) in pyridine (20 mL) at −20 °C. Large colorless crystals of the product (crystal system: tetragonal) were deposited (574 mg, 84%). The same stoichiometric product was also obtained from py/ACOH solutions (185 mg, 1.6%) from the filtrate at −20 °C.

**[Zn(O\(_2\)CCH\(_3\))]\(_2\)(py)\(_2\) (6).** Diethyl ether was slowly diffused to a solution of [Zn\(_2\)(O\(_2\)CCH\(_3\))]\(_2\)-2H\(_2\)O (342 mg, 1.0 mmol) in 10 mL of pyridine and 5 mL of acetic acid at −20 °C. Large colorless plates of the product (crystal system: monoclinic) were deposited (200 mg, 76%) (see also isolation of the product in reactivity studies). \(^{19}\)Fe NMR ([CD\(_3\)]\(_2\)SO): 8.58 (br, 2H, 3\(-\text{py}), 7.83 (tt, 1H, \(J_{\text{HH}} = 7.6 \text{ Hz}, 4\)-py-H)), 7.43 (m, 2H, 3-Hpy), 1.80 (s, 3H, CH\(_2\)CO). Anal. Calcld for C\(_{15}\)H\(_{17}\)N\(_2\)O\(_2\): C, 48.59; H, 4.60; N, 7.98.

**[Zn(O\(_2\)CCH\(_3\))]\(_2\)(py)\(_2\) (7).** A solution of [Zn\(_2\)(O\(_2\)CCH\(_3\))]\(_2\)-2H\(_2\)O (342 mg, 1.0 mmol) in ethanol (20 mL) or dichloromethane (20 mL) was evaporated to a small volume until colorless plates were apparent. The product was redissolved in situ upon mild heating and allowed to crystallize slowly (189 mg, 72%) at −20 °C. \(^{19}\)Fe NMR (CD\(_3\)CD\(_2\)OD): 8.57 (2H, 3\(-\text{py}), 7.81 (tt, 1H, \(J_{\text{HH}} = 7.8 \text{ Hz}, 4\)-py-H)), 7.41 (m, 2H, 3-Hpy), 1.79 (s, 6H, CH\(_2\)CO). Anal. Calcld for C\(_{15}\)H\(_{18}\)N\(_2\)O\(_2\): C, 47.21; H, 4.65; N, 7.18. Found: C, 47.87; H, 4.97; N, 7.45.

**[PPN][Fe\(_{1}\)(O\(_2\)CCH\(_3\))]\(_2\)(py)\(_2\) (9).** Compound 3 (300 mg, 0.61 mmol) and [PPN][Fe\(_{1}\)(O\(_2\)CCH\(_3\))] (360 mg, 0.60 mmol) were dissolved in 5.0 mL of pyridine upon stirring. The yellow-orange solution was filtered and diethyl ether was allowed to diffuse slowly into the filtrate at 20 °C. The yellow product crystallized as long needles (237 mg, 46%). \(^{19}\)Fe NMR ([CD\(_3\)]\(_2\)SO): \(\delta_{\text{H}} 67.64 \text{ (br, CH}_{2}\text{CO), 9.56 (s, br, 2-Hpy), 7.85 (t, } \(J_{\text{HH}} = 7.6 \text{ Hz, 4-Hpy}), 7.69 \text{ (t, } \(J_{\text{HH}} = 7.0 \text{ Hz, 3-Hpy}), 7.53 \text{ (2H, CH}_{2}\text{CO). IR (KBr): } \nu_{\text{C=O}} \text{ max} = 1643, 1586, 1428, 1311 \text{ cm}^{-1}.\)
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mm/s (ΔE0 = 2.97 mm/s, Γ = 0.25 mm/s). Anal. Calcld for C24H24N2Fe3O14S2: C, 28.34; H, 4.71; S, 9.37. Found: C, 28.43; H, 4.71; S, 9.46. Compound C4H12O3F3O6 (1) was dissolved in 27 mL of pyridine and 2.7 mL of acetic acid and allowed to react with 1 atm of pure dioxygen for 4 h. The solution was filtered, and the brown filtrate was reduced from which, a flame ionization detector, and a Hewlett-Packard 5890 Series II column equipped with a 25-m DB-Wax column and a Perkin-Elmer 9900 ChemStation. The products were identified by their UV-Vis (λmax = 396 nm). 57Fe Mössbauer (20 K): δ = 1.40 mm/s (ΔE0 = 2.94 mm/s, Γ = 0.02 mm/s, 34%). Anal. Calcld for C16H30Fe3O14S2: C, 64.6%; H, 5.98; N, 6.39. Found: C, 41.67; H, 5.84; N, 6.30.

Reaction of Ferrous Species with Dioxogen. The following compounds were isolated during investigations directed toward the elucidation of the reactivity of ferrous species with dioxogen.

[FeO(O2CCH3)(py)(O2)](1). Oxygen was admitted to a solution of compound 1 (300 mg, 0.61 mmol) in pyridine (20 mL) at −20 °C for 4 h. The solution was filtered, and the brown filtrate was reduced under vacuum to 10 mL. Diffusion of dioxogen into the filtrate at −20 °C afforded brown-black blocks of the product (150 mg, 86%). The product was obtained as large red-brown plates (crystal system: orthorhombic) of Zn[O2CCH3]2(py)2 (16). U V-MAS (1:1). KIE values were calculated for 1H NMR in (CD3)2CO/D2O following a reported protocol.29

Kinetic Isotope Effect Measurements. The intermolecular deuteron kinetic isotope effect was measured for adamantane by conducting catalytic oxidations (as previously described, but maintained at 25.0(1) °C with the aid of a Brinkmann R66 thermostat) on a mixture of adamantane/adamantane-d8 (1:1). KIE values were calculated for each product (average of three trials) from the ratio of protio/deuterio MS calculation of the relative intensities of the respective molecular ions selected over the fully resolved GC peaks. Corrections for the exact adamantane/adamantane-d8 ratio used, as determined by GC−MS, were applied.

X-ray Structure Determinations. Structures were determined for the compounds listed in Tables 1 and 2. Single crystals were picked from the reaction products, sealed in capillaries under an inert atmosphere and/or coated with Paratone-N oil, and transferred to a Siemens SMART (9) or a Nicolet P3 (all others) diffractometer. Lattice parameters were obtained from a least-squares analysis of more than 30 carefully centered reflections. None of the crystals showed significant decay during data collection. The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure factor amplitudes and their esd’s. An empirical absorption correction based on the observed variation in intensity of azimuthal (Ψ) scans was applied to the data sets for compounds 7, 9, and 11.
Space group assignments were based on systematic absences, $E$ statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and refined using either the SHELXTL PLUS 4.21/V or the SHELXTL 5.0 software package. Thermal parameters for all non-atom (1.5 times for methyl hydrogens). In the structure of hydrogen atoms were located from difference Fourier maps and refined using a riding model with isotropic thermal parameters. For all other structures, hydrogen atoms were assigned to ideal positions and refined using a riding model.

### Magnetic Measurements

Magnetic susceptibilities for the one-dimensional chain compounds 4 and 11 were obtained on a Quantum Design AC MRMS-55 SQUID magnetosusceptometer equipped with a 5.5 T magnet. Data were collected in the temperature range 2–300 K (total of 95 temperature points) at a field strength of 0.2 T and were corrected for the magnetization of the sample holder and for diamagnetic contributions as estimated from Pascal constants.

### Other Physical Measurements

$^1$H and $^{13}$C NMR spectra were recorded on Varian XL-400 and JEOL GXS-270 NMR spectrometers. The isotropically shifted peaks for the iron-containing compounds were assigned on the basis of chemical shift, integration, and selective deuteration. FT-IR spectra were obtained on a Perkin-Elmer 1800 FT-IR spectrometer. FT-near-IR spectra were recorded on a Bruker Vector 22 FT-near-IR spectrometer (Ge or InAs detectors) equipped with a fiber optic sample probe for near-IR/ATR spectra of solids. UV-visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Mössbauer data were recorded with a conventional Mössbauer spectrometer ($^{57}$Co source in a Rh matrix) operating at the constant acceleration mode and calibrated using a thin iron foil. Isomer shifts are reported relative to metallic iron at room temperature. SEM microprobe analysis was performed on a Jeol JEM-3010. Fibers and powders were inserted into a glass capsule filled with Ar gas to prevent oxidation.

### Table 1: Crystallographic Data for [Fe$_2$(O$_2$CCH$_3$)$_4$(py)$_2$](15)

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$^a$ Obtained at 295 K with a graphite monochromator Mo $\lambda$ ($\lambda = 0.71073$ Å) radiation. $^b$ $R = \sum ||F_o - |F_c||/\sum |F_o|$, $R_1 = \sum |w(F_o) - |F_c||/\sum |w(F_o)|^{1/2}$, $wR_2 = (\sum |w(F_o) - |F_c||/\sum |w(F_c)||)^{1/2}$.

### Table 2: Crystallographic Data for [Zn$_2$(O$_2$CCH$_3$)$_4$(py)$_2$](16), [Zn$_2$(O$_2$CCH$_3$)$_4$(py)$_2$](17), [Zn$_2$(O$_2$CCH$_3$)$_4$(py)$_2$](8), [PPN][Fe$_2$(O$_2$CCH$_3$)$_4$(py)$_2$](9), [Fe$_4$(H$_2$O)$_{24}$(trans-py)$_{24}$(O$_2$CCH$_3$)$_2$(py)$_{24}$(OS(CD$_3$)$_2$)$_{24}$(10), and [Fe$_4$(H$_2$O)$_{24}$(trans-py)$_{24}$(O$_2$CCH$_3$)$_2$(py)$_{24}$(OS(CD$_3$)$_2$)$_{24}$(11)

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$^a$ Obtained at 295 K with a graphite monochromator Mo $\lambda$ ($\lambda = 0.71073$ Å) radiation. $^b$ For definitions cf. Table 1. $^c$ $R_1$, $^d$ $wR_2$. 

Oxidation of Hydrocarbons under Gif-Type Conditions


Scheme 1

Results and Discussion

Reduction of Basic Iron/Zinc Acetates. With reference to Scheme 1, reduction of brown-black [Fe(II)(O2CCH3)6(py)3]-py (1)50 or dichroic red–green [Fe3O(O2CCH3)6(py)3]-py (1")51 with excess Zn in CH3CN/AcOH (10:1 or 2:1 v/v) or CH3Cl/AcOH (10:1), followed by Zn filtration, results in the precipitation of light yellow crystals of the air-sensitive compound [Zn2Fe2(O2CCH3)6(py)3]2 (1), upon cooling (−20 °C). The analogous reduction (0.5 h) of 1 (or 1") with Zn in py/AcOH (10:1 or 5:1) affords yellow-green crystals of [Fe2ZnO(O2CCH3)6(py)3]2 (2)53 directly from the reaction mixture at −20 °C. Evident in this reaction is the slow evolution of dihydrogen owing to the reaction of Zn with acetic acid. Prolonged (6 h) reduction results in a precipitation of light yellow crystals of the air-sensitive [Fe2ZnO(O2CCH3)6(py)3]2 (2)53 from py/AcOH (2:1) upon prolonged (>6 h) reduction of 1 (or 1") with Zn.

The inefficiency of catalytic Gif-type systems in pure pyridine prompted us to examine the reduction of 1 with excess Zn in the absence of AcOH. Prolonged (6 h) reduction results in a yellow-brown solution, from which compound 3 (80%) is obtained at −20 °C. From the supernatant, a small amount of a brown-black film precipitates upon diffusion of Et2O. Attempts to crystallize this material from organic solvents have been unsuccessful. Mössbauer data suggest that this species retains Fe(III), the amount of which is not diminished upon longer reaction times. However, employment of preactivated Zn dust (washed with HCl, CH3COOH, and pyridine) enables complete and rapid (0.5 h) reduction to yellow-green solutions from which the aforementioned Fe(II) species are obtained.

Pyridine-Dependent Equilibria. The pattern of isolation of the different species, which at first appeared erratic, suggests that multiple equilibria may be operative. These potentially include monomer/dimer equilibria for both iron and zinc species independently, as well as heterometallic cross-coupling equilibria (eqs 16–18).

2n[FeII(O2CCH3)2(py)3]2 (3) ⇌ [FeII(2O2CCH3)6(py)3]n (4) + (5n)py (16)
[FeII(O2CCH3)2(py)3]2 (3) + 2[Zn(O2CCH3)2(py)2] (5) ⇌ [Zn2FeII(O2CCH3)6(py)3]2 (2) + 6py (17)

In agreement with this interpretation, dilution of pyridine solutions with AcOH/Et2O or use of nonpyridine solvents in isolation procedures promotes an equilibrium shift in the direction 3 → 4 and 3(4) + 5 → 2. Further confirmation of the proposed equilibria is provided by the following control experiments which also serve as preparative methods. Compound 4 is obtained pure in the form of feathery crystals from saturated solutions of 3 in py/AcOH (5:1, 2:1) upon direct addition or diffusion of Et2O. However, crystals of 4 suitable for X-ray analysis (vide infra) could only be prepared from concentrated solutions of 3 in neat pyridine upon fast addition of Et2O (in order to avoid precipitation of 3) and subsequent slow diffusion of Et2O at 10 °C. Storage of the crystallization apparatus at lower temperatures favors precipitation of 3. Supersaturated solutions of 3 in pyridine at room-temperature deposit 4 as a yellow powder, although the latter is frequently contaminated with 3. Conversely, pure 4 can be precipitated by pyridine or py/AcOH solutions, from which 3 precipitates upon cooling (−20 °C).

In Gif-type solutions, equilibrium 17 lies predominantly on the left side. When dissolved in pyridine or py/AcOH (10:1, 5:1), light-yellow 2 affords intensely colored yellow-green solutions, from which essentially quantitative amounts of 3 and 5 are isolated upon cooling at −20 °C. Conversely, compound 3 and a 2-fold excess of 5 dissolved in pyridine or py/AcOH deposit light-yellow crystals of 2 upon addition of excess Et2O. In a similar fashion, 2 is recovered quantitatively from solutions containing both 3 and 5 in CH3CN, CH3Cl2, or DMSO.

Corroborative evidence for the pyridine-dependent equilibria among species 2–4 is provided by UV–vis spectra. Compound 3 demonstrates a characteristic charge-transfer absorption (λmax = 396 nm (ε = 2107) in py; λmax = 388 nm (ε = 2084) in py/AcOH (10:1); λmax = 368 nm (ε = 1900) in py/AcOH (2:1)) in the concentration range 10−5–10−4 M (Beer’s law observed; Figure 2 (top)). At higher concentrations (>1.0 × 10−3 M in py; >0.89 × 10−3 M in py/AcOH (10:1); >0.89 × 10−3 M in py/AcOH (2:1)), a new broad absorption appears (λmax = 424 nm in py; λmax = 406 nm in py/AcOH (10:1); λmax = 400 nm in py/AcOH (2:1)) and Beer’s law is no longer obeyed. At such high concentrations, the UV–vis criterion alone is not reliable

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Figure 2. (top) Optical spectrum of 3 (4.73 \times 10^{-4} \text{ M}) in pyridine. The inset shows the absorbance at 396 nm as a function of concentration. The arrow pinpoints to a solution of 2 (1.51 \times 10^{-4} \text{ M}) in pyridine. (bottom) Optical spectrum of 3 (1.86 \times 10^{-5} \text{ M}) in pyridine. The top inset shows the near-IR spectra of solid 2 (dotted line), 3 (dashed line), and 4 (solid line). The bottom inset shows the near-IR spectrum of a solution of 3 (1.02 \times 10^{-3} \text{ M}) in py/AcOH (10:1).

Evidence for the generation of new species in solution. However, in the near-IR region, solutions of 3 (10^{-3} \text{ to } 10^{-1} \text{ M}) or equimolar filtrates of the reduction of 1 by Zn powder in py or py/AcOH (10:1, 5:1, 2:1) demonstrate broad d-d transition bands (\( \lambda_{\text{max}} \approx 850 \text{ (}\epsilon_M \approx 8), 1180 \text{ (}\epsilon_M \approx 8) \text{ nm} \)) which are most closely related to those exhibited in n-IR/ATR spectra of solid 4 (Figure 2, bottom insets). We also note that the electronic spectrum of 2 (10^{-5} \text{ to } 10^{-3} \text{ M}) in pyridine or py/AcOH (10:1, 5:1, 2:1) is identical with that exhibited by 3/4 and accounts for greater than 90\% conversion of 2 to 3/4 (Figure 2, top inset). These results suggest that addition of Et\(_2\)O or employment of nonpyridine solvents is essential for the generation of 2.

The precise nature of species 4 in pyridine or py/AcOH solutions is not easily discernible. It is unlikely that infinite chains of 4 will be present in solution, although the degree of aggregation can be substantial in the polar py/AcOH matrix.55 However, electrospray MS data obtained at various initial concentrations of 3 in py/AcOH (10:1) have only yielded fragments assigned to [Fe(OAc)(py)]\(^+\), [Fe(OAc)(py)\(_2\)]\(^+\), [Fe\(_2\)-(OAc)(py)]\(^+\), [Fe\(_2\)-(OAc)(py)\(_2\)]\(^+\), [Fe\(_3\)-(OAc)\(_3\)(py)]\(^+\), and [Fe\(_3\)-(OAc)\(_3\)(py)\(_2\)]\(^+\)]. The trigonal fragments become apparent at higher initial concentrations (\([I3] \geq 0.88 \times 10^{-3} \text{ M})\), although the effective concentration of 3 in the droplet (travelling against a countercurrent of inert gas) from which the ions desorb is not known. \(^1\)H NMR spectra of 3 in pyridine or py/AcOH are not very informative, even at low temperatures, owing to the rapid exchange of pyridine/acetate moieties among the various iron-containing species and the solvent matrix. In CH\(_2\)Cl\(_2\) (as well as in other non-pyridine solvents), chemical shifts for pyridine/acetate groups of 3/4 are concentration-dependent, the degree of isotopic shift diminishing with decreasing concentration. It is noteworthy that 3 is crystallized from saturated solutions of 3 in CH\(_2\)Cl\(_2\), while diffusion of Et\(_2\)O into CH\(_2\)Cl\(_2\) affords a microcrystalline product that is analytically identical to compound 4. Antiferromagnetically coupled dinuclear and higher nucularity species are expected to demonstrate isotropically shifted NMR spectra of reduced range by comparison to their mononuclear counterparts.

The slow reaction of Zn with AcOH results in the formation of solubilized zinc acetate products which participate in equilibria in parallel to, as well as along with iron species. Compound 5 is consistently obtained along with other iron-containing species from pyridine or py/AcOH (10:1, 5:1) Gif-type solutions. It can also be crystallized pure from similar solutions of Zn(O\(_2\)CCH\(_3\))\(_2\)\(\cdot\)2H\(_2\)O, albeit in two distinct crystal systems: tetragonal in pyridine or py/AcOH (10:1) and triclinic from py/AcOH (5:1). The aforementioned dissociation of 2 in pyridine or py/AcOH (10:1) to generate 3 and 5 also affords crystals of 5 in the tetragonal crystal system. However, solutions of 5 in py/AcOH (2:1) yield exclusively [Zn\(_2\)(O\(_2\)CCH\(_3\))\(_2\)(py)\(_2\)]\(^+\) (6) upon crystallization. Compound 6 usually crystallizes in the monoclinic system, although on a single occasion it has also been crystallized from py/AcOH (2:1) in the orthorhombic crystal system, as one of the products of the oxidation of 2 (vide infra). Variable-concentration and -temperature \(^1\)H NMR spectra of 5 in pyridine or py/AcOH are not sufficiently diagnostic, most likely due to rapid ligand exchange even at low temperatures. However, CI-MS data reveal that the molecular ion of 5 (\(m/z = 341.7\)) and fragments of 6 are solely detected from py/AcOH solutions, the latter being more pronounced for samples in py/AcOH (2:1). It thus appears that, in Gif-type solutions, zinc is present in the form of 5 and 6. Higher nucularity species have been detected and isolated only from non-pyridine solvents. The one-dimensional chain compound [Zn\(_2\)(O\(_2\)CCH\(_3\))\(_2\)(py)\(_2\)]\(^+\) (7) is obtained from solutions of 5 in EtOH or CH\(_2\)Cl\(_2\), while the trinuclear [Zn\(_3\)(O\(_2\)CCH\(_3\))\(_6\)(py)\(_2\)]\(^+\) (8) is deposited from solutions of 5 in CH\(_3\)CN or 6 in CH\(_2\)Cl\(_2\). As in the case of 4, the nature of 7 in solution is not precisely known, but interestingly, this species is isomeric to 6.

**Other Reducing Agents.** Although Zn dust is the most practical source of reducing equivalents, compounds 3 and 4 can also be isolated by treatment of 1 with excess iron dust in pyridine or py/AcOH (10:1) for 30 min and from the reaction of 1 with Hz (30 psig)/Pd in pyridine or py/AcOH (10:1) for 1 h. Both reactions, after removal of insoluble components, afford bright yellow-green solutions from which high yields of compounds 3/4 are crystallized as previously described. A control experiment confirmed that these species are also generated by simply stirring Fe in py/AcOH (10:1). Iron has been previously used as a reducing agent in the early Gif systems: tetragonal in pyridine or py/AcOH (5:1) and triclinic in CH\(_2\)Cl\(_2\), while the tetragonal Gif systems: tetragonal in pyridine or py/AcOH (10:1) and triclinic in CH\(_2\)Cl\(_2\). (b) Barton, D. H. R.; Motherwell, R. C; Motherwell, W. B. J. Chem. Soc., Chem. Commun. 1983, 41–43. (b) Barton, D. H. R.; Motherwell, R. S. H.; Motherwell, W. B. Tetrahedron Lett. 1983, 1979–1982.

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Attention, since addition of water to py/AcOH (10:1) up to an optimum amount of 6.6% w/w is known to enhance the selectivity of Gif chemistry.

Addition of [Ph3P=N=Ph3P][O2CCH3] (1 equiv) to 3 in pyridine affords yellow needles of [PPN][Fe4(O2CCH3)3(py)] (9) upon diffusion of Et2O at room temperature. In contrast, a mixture of predominantly 3 and a minor amount of 9 are deposited directly from concentrated pyridine solution at 20 °C. Solutions of 3 in pyH2O (10:1) or py/AcOH/H2O (10:1:0.7) afford yellow crystals of [Fe4(H2O)4(μ-OAc)2][O2CCH3]2(10) upon slow diffusion of Et2O. Compound 10 reverses quantitatively to 3 in neat pyridine as evidenced by isolation of 3 (−20 °C). UV–vis spectra of 10 in pyridine or pyH2O exhibit features identical to those observed for 3 ([λ]10 < 1.0 × 10⁻³ M), indicating complete dissociation of the water adduct in favor of the pyridine-ligated species.

The lability of pyridine is also demonstrated thermogravimetrically in its facile thermal (50 °C) dissociation from 3 under vacuum (0.01 Torr), leading to the successive loss of two (1.5 h), three (2.5 h), and finally four (6 h) pyridine equivalents to yield Fe(OAc)2. The purity and identity of the intermediate products cannot be easily elucidated, since employment of non-pyridine solvents to dissolve these species further contributes to pyridine dissociation. This is dramatically shown in the case of the prolonged incubation of 3 in DMSO-d₆ that leads to precipitation of colorless, air-sensitive crystals of [Fe₄(O₂CCH₃)₆(OH)₄(py)₃][Fe(OAc)₂]. The purity and identity of the intermediate are not sufficient for complete occupancy of the divalent site of the µ-oxo structure by zinc after oxidation.

Admittance of dioxygen to the filtrate of the prolonged reduction (6 h) of 1 by Zn in pyridine deposits dichroic red–green crystals of monoclinic 1'. Interestingly, compound 1', prepared by the original method, crystallizes in the rhombohedral crystal system. The isolation of 1' indicates that, in catalytic oxidations in which excess Zn is in contact with py/AcOH (10:1) for 18 h, compound 1' may be more involved as the product of autoxidation than the all-iron species 1.

Solid State Structures. (a) Iron Species in Gif Solutions.
Among the various stoichiometries reported, only species 1/1' and 3/4 can be legitimately claimed to be present in pyridine or py/AcOH solutions, with the aforementioned reservations in regards to the precise nature of 4 in these solutions taken into account. Compound 1' (Figure 3, top) crystallizes in space group R₃2, featuring trinuclear metal µ-oxo clusters with crystallographically imposed D₃h symmetry. The occupancy of each metal site was fixed at Fe 0.37 and Zn 0.13, based on analytical data. Disorder of the trinuclear unit at 223 K does not allow the different metal sites to be distinguished. Each M–O(1) vector (1.914(1) Å) lies along a Cₐ axis, while O(1) resides on a perpendicular C₃ axis. As previously revealed in similar structures, the solvated pyridine is sandwiched along the C₃ axis between two stacked trinuclear clusters and is severely disordered. In contrast, the structure of compound 1'' (Figure 3, bottom), synthesized by the in situ oxidation of reduced (6 h) solutions of 1 by Zn in pyridine (vide supra), displays the more rarely observed monoclinic crystal system that, lacking a C₃ axis, distinguishes between two metal sites by virtue of a crystallographically imposed C₂ axis. This axis penetrates atoms O(1'), M(2), N(2), and C(14). M(1) and M(2) represent metal sites of occupancy Zn(1/3)Fe(2/3) and Zn(1/3)Fe(1/3), respectively. The M(1)–O(1) vectors (1.292(3) Å) are slightly longer than the unique M(2)–O(1) vector (1.900–6(Å) but not sufficiently different to allow exclusive assignment of M(1) and M(2) to sites Fe(III) and Zn(II), respectively.

The structure of mononuclear 3 (Figure 4) reveals a distorted octahedral Fe environment with an imposed C₃ axis residing in the equatorial plane defined by the four Fe–N bonds and bisecting the symmetry-related N(1)–Fe–N(1') (89.1(2)°) and N(2)–Fe–N(2A) (92.2(2)°) angles. Pyridine rings are arranged in a propeller fashion around the equatorial plane. Relevant to the observed distortion are the Fe–N(1) and Fe–N(2) bond distances as well as the O(1)–Fe–N(1) and O(1)–Fe–N(2) bond angles which slightly differ from each other. The most visible sign of the distortion is the departure from linearity of the angle between the two trans acetate groups along the propeller axis (O(1)–Fe–O(1') = 168.5(2)°).

The structure of 4 (Figure 5) reveals a one-dimensional polymer chain comprised of asymmetric diferrous units. In the unit cell, the chains run parallel to the 2₁ screw axis (along the

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The elongation along the Fe(1) atom is coordinated by two N(py) donor atoms via O(8) and O(7A) (Fe(1)–M(2) 2.076(4), Fe(2)–O5 2.175(4), Fe(1)–O(5) 2.179(4), Fe(1)–N(1) 2.228(4), Fe(1)–N(2) 2.247(4), Fe(2)–O(2) 2.033(4), Fe(2)–O(4) 2.117(4), Fe(2)–O(5) 2.212(3), Fe(2)–N(3) 2.259(5), Fe(2)–O(6) 2.273(5), O(7)–Fe(1)–O(1) 92.9(2), O(3)–Fe(1)–O(1) 90.6(2), O(1)–Fe(1)–O(5) 92.6(2), O(5)–Fe(1)–N(1) 178.6(1), O(1)–Fe(1)–N(2) 175.4(2), O(2)–Fe(2)–O(5) 96.00(14), O(8A)–Fe(2)–O(5) 142.76(14), O(2)–Fe(2)–O(6) 152.9(2), O(4)–Fe(2)–O(6) 93.7(2), O(5)–Fe(2)–O(6) 57.4(2), N(3)–Fe(2)–O(6) 88.7(2).

Figure 5. Structure of the local dinuclear geometry (top) and one-dimensional chain (bottom) of [Fe(CH$_3$COO)$_2$(py)$_4$]$_2$ (4) showing 30% probability ellipsoids and the atom labeling scheme. Selected interatomic distances (Å) and angles (deg): Fe(1)–O(7) 2.073(4), Fe(1)–O(3) 2.076(4), Fe(1)–O(1) 2.157(4), Fe(1)–O(5) 2.179(4), Fe(1)–N(1) 2.228(4), Fe(1)–N(2) 2.247(4), Fe(2)–O(2) 2.033(4), Fe(2)–O(4) 2.117(4), Fe(2)–O(5) 2.212(3), Fe(2)–N(3) 2.259(5), Fe(2)–O(6) 2.273(5), O(7)–Fe(1)–O(1) 92.9(2), O(3)–Fe(1)–O(1) 90.6(2), O(1)–Fe(1)–O(5) 92.6(2), O(5)–Fe(1)–N(1) 178.6(1), O(1)–Fe(1)–N(2) 175.4(2), O(2)–Fe(2)–O(5) 96.00(14), O(8A)–Fe(2)–O(5) 142.76(14), O(2)–Fe(2)–O(6) 152.9(2), O(4)–Fe(2)–O(6) 93.7(2), O(5)–Fe(2)–O(6) 57.4(2), N(3)–Fe(2)–O(6) 88.7(2).

Figure 3. Structures of trigonal [Fe$_2$(O$_2$CCH$_3$)$_3$(py)$_4$](1) (top) and monoclinic [Fe$_2$ZnO(O$_2$CCH$_3$)$_3$(py)$_4$](1) (bottom) showing 40% and 30% probability ellipsoids, respectively and the atom labeling scheme. Selected interatomic distances (Å) and angles (deg) for 1': M–O(1) 1.914(1), M–O(2) 2.042(5), M–N(1) 2.203(7), O(1)–M–O(2) 96.2(2), O(1)–M–N(1) 180.0(1), O(2)–M–N(1) 83.8(2); 1': M–O(1) 1.929(3), M–O(2) 2.057(6), M–O(4) 2.075(6), M–N(1) 2.202(9), M–O(1) 1.900(6), M–O(3) 2.072(7), M(2)–O(5) 2.041(6), M(2)–N(2) 2.211(8), O(1)–M(1)–O(2) 96.2–3(3), O(1)–M(1)–O(4) 95.3(3), O(2)–M(1)–O(4) 89.1(3), O(1)–M(1)–N(1) 179.7(2), O(1)–M(2)–O(3) 95.3(2), O(1)–M(2)–O(5) 96.2(2), O(3)–M(2)–O(5) 89.8(3), O(1)–M(2)–N(2) 180.0(1), M(1)–O(1)–M(2) 120.2(2).

Figure 4. Structure of the mononuclear [Fe$_{111}$(O$_2$CCH$_3$)$_3$(py)$_4$] (3) compound showing 50% probability ellipsoids and the atom labeling scheme. Selected interatomic distances (Å) and angles (deg): Fe–O(1) 2.031(4), Fe–N(1) 2.240(5), Fe–N(2) 2.213(5), O(1)–Fe–N(1) 85.8(2), O(1)–Fe–N(2) 94.1(2), N(1)–Fe–N(2) 89.4(2), O(1)–Fe–O(1A) 168.5(2).

c axis). Each dinuclear unit is bridged to two adjacent units via O(8) and O(7A) (Fe(1)–Fe(2') = 5.275 Å). The essentially octahedral Fe(1) atom is coordinated by two N(py) donor atoms and four acetate-derived oxygen atoms, featuring a slight elongation along the O(1)–Fe(1)–N(2) direction. The much more distorted Fe(2) site is surrounded by an O$_5$/N ligating environment. The two iron atoms of the asymmetric core (Fe(1)–Fe(2) = 3.676 Å) are bridged by two bidentate acetate groups and a unique monodentate acetate bridge which also serves as a bidentate chelator to Fe(2). The metric parameters associated with the shift from a bridging monodentate to an ancillary chelating position (termed “the carboxylate shift”) have been discussed in the literature,60 the degree of the “shift” varying with the extent of contact of the distal oxygen atom with the iron site. The one observed in Fe(2)–O(6) = 2.273(5) Å is a rare case of a strong bonding interaction (comparable to Fe(2)–O(5) = 2.212(3) Å), instances of which are only found in the structures of Fe$_3$(O$_2$CPh)$_6$L$_2$ (L = PrOx, PhMe$_2$Eda),61 the dimetallic Mn(II)Ca(II) site of concanavalin A,62 and, more importantly, the diiron site of the H$_{red}$ component of sMMO (Fe–O(Glu243) = 2.33 Å).6a,b Indeed, the corresponding Fe(2) sites of 4 and H$_{red}$ in sMMO demonstrate remarkable metrical similarities with respect to the arrangement of their respective O$_5$/N coordination sphere, although the sMMO site is closer to being five-coordinate. The most pronounced difference is the existence of a weakly bound semibridging water molecule in H$_{red}$ in lieu of a bridging bidentate acetate in 4. The monodentate water bridge may be responsible for the relative shrinkage of the reported Fe–Fe distance (3.28 Å) in H$_{red}$ versus the corresponding distance in 4. The coordination sphere of
Fe(1) in 4 differs from the corresponding site in \( H_{\text{red}} \) both in being more nitrogen-rich and in the relevant orientation of the bridging versus the terminal residues.

(b) Other Ferrous Acetate Structures. The structure of 2 (Figure 6) reveals a linear arrangement of three metal sites, featuring an essentially octahedral centrosymmetric iron atom bridged to two tetrahedrally ligated zinc atoms. The bridging moieties are provided by two bidentate and one monodentate acetate groups. A slight elongation along the O(31)−Fe(1)−O(31′) axis (Fe(1)−O(31) = 2.156(3) Å) of the exclusively oxygen-coordinated iron site is observed. The tetrahedral geometry of the outer zinc atoms is distorted, especially with respect to the position of the bridging oxygen atom of the monodentate acetate group versus the nitrogen atom of pyridine (O(31)−Zn(1)−N(1) = 129.2(1)°). A similar arrangement of bridging acetate groups has been observed in homonuclear and heteronuclear \( M_2 M' O(CCR_3)_3 \) \( L_2 \) structures (\( M = V, Mn, Fe, Co, Zn; M' = V, Mn, Fe, Co, Ni, Zn, Cd, Mg, Ca, Sr; L = substituted pyridines or bidentate N-donor ligands)\(^{6b} \) although the ZnFe combination was unknown. Of particular interest in this series of compounds are the aforementioned trinuclear iron species of stoichiometries Fe\(_3\)(O\(_2\)CCR\(_3\))\(_3\)\( L_2 \) structures (\( M = V, Mn, Fe, Co, Zn; M' = V, Mn, Fe, Co, Ni, Zn, Cd, Mg, Ca, Sr; L = substituted pyridines or bidentate N-donor ligands)\(^{6b} \) in which the outer iron atoms are additionally coordinated (weakly or strongly) by the distal oxygen atom of the monodentately bridging acetate.

The structure of compound 9 (Figure 7) reveals a pseudo-seven-coordinate iron center coordinated by three asymmetrically chelating acetate groups and a unique pyridine moiety. The asymmetry of the bidentate chelation is evident from the Fe−O(1) (2.087(3) Å) and Fe−O(2) (2.315(3) Å) distances and becomes more pronounced with the other two acetates, since both O(4) and O(6) assume positions of interatomic contact with the iron center (Fe···O(4/6) = 2.829 Å).

The structure of compound 10 (Figure 8) reveals an octahedral iron site residing on an inversion center and coordinated by four water molecules in the equatorial plane and two pyridine molecules along a perpendicular axis. All hydrogen atoms, with the exception of those on the Me group of the acetate, were located in the electron density map and refined isotropically. Each hydrogen atom belonging to a coordinating water molecule makes a hydrogen bond with an acetate oxygen atom. The two noncoordinating acetates associated with the cationic iron center form hydrogen bonds with cis-water molecules in a bidentate fashion (O(3)−H(1A) = 1.92 Å, O(4)−H(2A) = 1.91 Å; O(3)−O(1) = 2.680 Å, O(4)−O(2) = 2.680 Å). In addition, each acetate is hydrogen-bonded to two adjacent cationic units (O(3)−H(1B) = 1.98 Å, O(4)−H(2B) = 2.00 Å), leading to an overall two-dimensional sheet network structure.

(c) Structures of Zn-Containing Species. Two crystallographic versions of 5 have been obtained. Presumably, they represent closely spaced energetic minima. The compound obtained in the tetragonal space group \( P4_2 2_2 \) (Figure 10, top), reveals a tetrahedral zinc site residing on a crystallographically imposed \( C_2 \) axis bisecting the N−Zn−N(A) (110.7(3)°) and O(1)−Zn−O(1A) (98.0(3)°) angles. Distortions from tetrahedral

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**Figure 6.** Structure of the centrosymmetric compound \([\text{Zn}_2\text{Fe}^{II}\text{O}_2\text{CCH}_3]_{3}\)(py)\(_2\)) (2) showing 40% probability ellipsoids and the atom labeling scheme. Selected interatomic distances (Å) and angles (deg): Fe(1)−O(12) = 2.115(3), Fe(1)−O(22) = 2.099(3), Fe(1)−O(31) = 2.156(3), Zn(1)−O(11) = 1.954(3), Zn(1)−O(21) = 1.942(3), Zn(1)−O(31) = 1.959(3), Zn(1)−N(1) = 2.017(4), O(12)−Fe(1)−O(22) = 94.1(1), O(12)−Fe(1)−O(31) = 91.5(1), O(11)−Zn(1)−O(21) = 112.0(1), O(11)−Zn(1)−O(31) = 105.3(1), O(31)−Zn(1)−N(1) = 129.2(1). \( \text{Zn}^2\text{−Zn}^2\text{−Fe}^{II} \)

**Figure 7.** Structure of the anionic component of \([\text{PPN}]^+\text{[Fe}^{II}\text{O}_2\text{CCH}_3\text{)}\_2((-py)\_2)]^−\) (9) showing 30% probability ellipsoids and the atom labeling scheme. Selected interatomic distances (Å) and angles (deg): Fe−O(5) = 2.033(4), Fe−O(3) = 2.059(4), Fe−O(1) = 2.087(3), Fe−O(2) = 2.313(3), Fe−N(1) = 2.160(4), O(5)−Fe−O(3) = 90.1(2), O(5)−Fe−O(1) = 135.3(2), O(3)−Fe−O(1) = 129.5(2), O(5)−Fe−N(1) = 99.3(2), O(3)−Fe−N(1) = 104.0(2), O(1)−Fe−N(1) = 90.8(2), O(5)−Fe−O(2) = 104.0(14), O(3)−Fe−O(2) = 94.9(14), O(1)−Fe−O(2) = 59.0(13), N(1)−Fe−O(2) = 149.7(2).

**Figure 8.** Structure of the local environment of the cation (left) and 2-D sheet network (right) of centrosymmetric \([\text{Fe}^{II}\text{H}_2\text{O}_4\text{trans-py}]^+\text{[O}_2\text{CCH}_3\text{]}^2\) (10) showing 40% probability ellipsoids and the atom labeling scheme. Selected interatomic distances (Å) and angles (deg): Fe−O(1) = 2.122(2), Fe−O(2) = 2.122(2), Fe−N(1) = 2.213(2), O(1)−Fe−O(2) = 90.32(10), O(1)−Fe−N(1) = 92.83(10), O(2)−Fe−N = 92.67(10).

The crystal structure of 11 (Figure 9) was obtained from a crystal grown in solutions of DMSO-\( d_6 \). The compound is a one-dimensional solid containing chains comprised of two types of iron in a 2:1 (Fe(1):Fe(2)) ratio. Two Fe(1) centers are intimately coupled by one bidentate and two monodentate acetate bridges (Figure 9, top), although each of the distal oxygens of the monodentate acetate groups coordinates to an adjacent Fe(2) site. A crystallographically imposed \( C_2 \) axis penetrates atoms C(7) and C(8) of the bidentate acetate group. In addition, each Fe(1) is coordinated by one DMSO and two acetate groups. The latter are both bridging to the adjacent unique Fe(2) site (Figure 9, middle). One of them is a typical bidentate acetate, while the other is a unique monodentate bridge which also acts as a chelator to Fe(2). By virtue of a \( C_2 \) axis passing through atoms Fe(2), C(5), and C(6), the latter oxygen is also bridging the iron sites of the adjacent Fe(1)\(_2\) unit; thus, this acetate spans the range Fe(1)···Fe(2)···Fe(1)\(_2\) (Figure 9, bottom).
symmetry are made evident by the latter angle and are likely due to two long-range $\text{Zn} \cdots \text{O(2)}$ interactions. Compound 5 crystallized in the triclinic space group $P\overline{1}$ with a slightly different geometry (Figure 10, bottom). The two structures differ primarily in the relative positions of the two long-range $\text{Zn} \cdots \text{O}$ contacts.

Crystals of compound 6 are also obtained in two crystallographic versions. In its monoclinic form, the dinuclear molecule (Figure 11) resides on a $C_2$ axis which penetrates atoms C(7), N(1), Zn(1), Zn(2), N(2), and C(10). In its orthorhombic form (see Supporting Information), the compound lies on an inversion center midway along the internuclear axis. The only noteworthy difference between the two structures lies in the torsion angles made by the planes of the two axial pyridine ligands.

The structure of compound 7 (Figure 12) reveals an extended one-dimensional solid comprised of an array of five-coordinate zinc centers. The chain repeat unit is defined by two zinc centers, Zn(1) and Zn(2). Each zinc atom is bridged to two neighbors by a bidentate acetate and is further coordinated by a pyridine and an asymmetrically chelating acetate group. Pyridine rings are oriented nearly perpendicular to each other at adjacent Zn sites. Most importantly, the chelating acetate groups are nonequivalent and asymmetric at these Zn centers (Zn(1)–O(1) = 2.024(6) Å, Zn(1)–O(2) = 2.414(7) Å; Zn(2)–O(3) = 2.116(6) Å, Zn(2)–O(4) = 2.255(7) Å).

Compound 8 (Figure 13) is isomorphous with 2, featuring a trinuclear zinc molecule residing on an inversion center. The unique octahedral zinc atom is bridged via two bidentate
one monodentate acetate groups to the outer tetrahedral zinc sites. Metric parameters are virtually identical with those observed in 2. Structures similar to 6 and 8 have been reported for compounds of stoichiometry Zn_{2}(carboxylato)_{4}(base)_{2} and Zn_{3}(carboxylato)_{6}(base)_{2}, respectively.²⁻³

**Mössbauer Spectroscopy and Magnetization Studies.** All iron-containing compounds presented in this investigation have been studied by $^{57}$Fe Mössbauer spectroscopy. The zero-field spectra of the ferrous pyridine/acetate compounds (2–4 and 9–11) exhibit quadrupole doublets at isomer shifts and quadrupole splitting parameters characteristic of high-spin ferrous sites ($S = 2$). The isomer shift values for the neutral species 2–4 and 11 indicate a trend that is consistent with increasing $\delta$ values as the amount of oxygen ligation increases versus nitrogen ligation. This trend has been previously suggested for Fe(III) species. Even in the case of the asymmetric diiron site of 4, the zero-field Mössbauer spectrum in the solid state at 4.2 K (Figure 14, top) demonstrates a unique quadrupole doublet ($\delta = 1.27$ mm/s, $\Delta E_Q = 2.92$ mm/s, $\Gamma = 0.20$ mm/s), thus the two iron sites remain indistinguishable even at low temperature.⁶⁴ In contrast, the Mössbauer spectrum of 11 shows a substantially broadened and rather asymmetric quadrupole doublet (Figure 14, bottom). The spectrum can be successfully fitted by virtue of two different ferrous sites at a ratio of 2:1 ($\delta = 1.40$ mm/s, $\Delta E_Q = 3.04$ mm/s, $\Gamma = 0.20$ mm/s, 66%; $\delta = 1.38$ mm/s, $\Delta E_Q = 2.94$ mm/s, $\Gamma = 0.22$ mm/s, 34%).

The measured magnetic susceptibility per iron of 4 as a function of temperature is shown in Figure 15. The $\mu_{eff}$ value of 4 at room temperature is 5.0 $\mu_B$, close to the value expected for uncoupled Fe(II) ions. The molar susceptibility, $\chi_M$, increases with decreasing temperature reaching a local maximum at 10 K ($\chi_M = 0.1012$ emu mol⁻¹). At lower temperatures, $\chi_M$ again increases, probably due to the presence of a paramagnetic impurity.
As mentioned earlier, the structure of 4 shows two largely different Fe⋯Fe distances (3.676 and 5.275 Å), and therefore, alternation of exchange coupling constants is anticipated. The shorter bridge, comprised of two bidentate and one monodentate as well as chelating acetate groups, is expected to be more efficient than the longer one in transmitting the magnetic interaction. The geometry between the closely spaced Fe ions is similar to that found in other metal ion dimers\(^{61,66}\) and is known to mediate a small magnetic exchange between ferrous sites.\(^{61}\) In contrast, the single bidentate acetato group, bridging the longer Fe⋯Fe separation, is expected to be very ineffective in transmitting exchange interactions. On this basis, magnetic data were first analyzed by using a simple dinuclear model, that is, setting the coupling constant along the longer bridge to zero. The magnetic susceptibility data were fitted to the analytical expression derived from the isotropic Heisenberg–Dirac–van Vleck model using the spin Hamiltonian 19 which consists of three terms describing the isotropic exchange, axial zero-field local anisotropy and Zeeman perturbation.

\[
\hat{H} = -J S_1 S_2 + \frac{2}{\gamma} \sum_{i=1}^{2} (S_i^2 - S_i(S_i + 1)/3) + \mu_B g S_i \hat{H} \quad (19)
\]

The best fit of molar susceptibility data is shown in Figure 15 as a solid line and corresponds to \(g = 2.077, J = -3.36\) cm\(^{-1}\), and \(D = -1.441\) cm\(^{-1}\). The paramagnetic impurity was evaluated as 4.45 wt % of Fe(III) (\(S = \frac{3}{2}\)), assuming oxidative decomposition of this exceedingly air-sensitive compound. The \(J\) value so obtained is in good agreement with values determined for similar, antiferromagnetically coupled compounds (\(-20 \leq J \leq 0\) cm\(^{-1}\))\(^{61,65}\) and in particular with small values (\(J = -1.0\) cm\(^{-1}\)) reported for the similarly bridged species Fe\(_2\)(O\(_2\)CPb)\(_2\)L\(_2\) (\(L = \text{PrOx, PheMeE}da\)).\(^{61}\) The \(D\) value is also close to those reported for mononuclear zero-field splitting at individual sites of dinuclear ferrous systems.\(^{65}\) Attempts were also made to analyze the data by means of a homogeneous chain model.\(^{67}\) The spin Hamiltonian (eq 20) used to describe the magnetic interaction between adjacent ions in a regular magnetic chain and the analytical expression\(^{68}\) (eq 21) employed to fit the data are as follows:

\[
\hat{H} = -J \sum_{i=1}^{\infty} S_i S_{i+1} + A T_i + B + C T_i^2 + D T_i^4 + E 
\]

\[
\chi_r = \frac{3J^2/|J| \lambda g^2 S(S+1)}{3 + C T_i^2 + D T_i^4 + E} 
\]

where \(\chi_r = 3\gamma_J |J|\lambda g^2 S(S+1)\) and \(T_i = kT_i/|J|\) are the reduced susceptibility and temperature, respectively. The analytical expression is obtained by an extrapolation procedure on data calculated for closed chains (rings) of increasing size from 3 to 6 metal sites; a six-ion ring is the upper limit for \(S = 2\) ions, due to the computational effort involved.

The fit with the six-metal model \((g = 2.059(3), J = -2.011\) (7) cm\(^{-1}\)) was less satisfactory by comparison to the one obtained with the dinuclear model, confirming the suggestion that the two magnetic coupling constants, along the shorter and longer Fe⋯Fe distances, must be substantially different from each other. Unfortunately, analytical formulas for alternating chains of \(S = 2\) ions are not currently available.

The \(\mu_{\text{eff}}\) value of 11 at room temperature is 5.3 \(\mu_B\) per ferrous ion, in agreement with independent spins. On decreasing temperature, \(\mu_{\text{eff}}\) remains essentially constant down to ca. 10 K, rapidly decreasing beyond that point (see Supporting Information). The susceptibility \(\chi_M\) continuously increases with decreasing temperature, but no maximum is observed, suggesting that the exchange coupling, if any, is close to zero.

Since the structure of 11 reveals similar Fe⋯Fe separation distances between neighboring ferrous sites (3.267, 3.543 Å), attempts were made to fit the magnetic data with the homogeneous chain model, even though the bridging geometry is different in the two cases. The parameters thus obtained are \(g = 2.18(1)\) and \(J = -0.22(1)\) cm\(^{-1}\), but the fit (see Supporting Information) was quite poor for the data at lower temperatures. To our knowledge, no other models are available for a magnetic system of this complexity, the fitting being even more difficult due to the weakness of the magnetic interaction. No further attempts were undertaken to improve on the fitting procedure.

**Catalytic Oxidations.** Oxidation of adamantane mediated by \(2\) under Gif-type conditions affords the following products (unless otherwise specified, percentages are based on mol % of substrate conversion): 2-adamantanone (\(2, 10.7\%\); 3, 10.7\%); 2-adamantanol (\(2, 1.2\%\); 3, 1.3\%); 1-adamantanol (\(2, 0.8\%\); 3, 0.9\%); 4-(1-adamantyl)pyridine (\(2, 6.0\%\); 3, 5.9\%); 4, 6.0\%); and 2-(1-adamantyl)pyridine (\(2, 3.8\%\); 3, 4.0\%); 4, 3.2\%). Traces of 4-(2-adamantyl)pyridine and 2-(2-adamantyl)pyridine are also observed. Oxidation of 2-adamantanediol mediated by 1 affords only 6.9\% of 2-adamantanone under identical conditions. Oxidation of adamantane by \(\text{I}_2/\text{ZnO}\) in \(\text{CH}_3\text{CN}/\text{AcOH}\) (10:1) yields low conversions of 1-adamantanone (2.8\%), 2-adamantanone (1.2\%), and 2-adamantanone (0.8\%). Acceptable mass balances are larger than 95\% in all cases.

These values are comparable to those previously reported\(^{65}\) for 1 and are further indicative of the equivalence of species \(1\)–\(4\) in catalytic solutions; this fact was anticipated due to the observed pyridine-dependent interconversions. The normalized \(3^\text{rd}\) preference on a per-hydrogen basis gives an average value of 2.65 for Gif-type oxidations. The selectivity for the tertiary position \((3^\text{rd}) = 4.2\) increases for oxidations in \(\text{CH}_3\text{CN}/\text{AcOH}\), at the expense of lower yields achieved. These values can be compared with values of 11–48 for oxidation of adamantane by P-450 mimics (depending on porphyrin substitution) coupled to \(\text{PhiO}\).\(^{69}\) 20 for generic radical reactions of adamantane.\(^{70}\) 10 for radical reactions (\(t\)-BuO\(^\circ\)) of adamantane in pyridine\(^{70}\) (albeit 2.7 for chlorination with \(t\)-BuOCl),\(^{31}\) 10 for oxidation of adamantane by \(\text{Fe}_2\text{O}(2,2\text{-bipy})_\text{2}(\text{H}_2\text{O})_4(\text{ClO}_4)_4/\text{t}-\text{BuO}OH\) in \(\text{CH}_3\text{CN}\),\(^{15}\) 9.5 for oxidation of adamantane by \([\text{FeCl}_2-\text{TPA})\text{ClO}_4/\text{t}-\text{BuO}OH\) or \(\text{CumOOH}\) in \(\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}\) (1:1),\(^{13}\) 3–10 for oxidation of adamantane by Mn-porphyrin/KHOSO\(_4\).

by employing the 3 shown to substantially increase in the presence of PPh₃ in the cleavage. Importantly, the KIE value for cyclohexanol has been influenced by the initial C

Typically, the KIE value for oxidations by HO* is 1.72. However, values close to unity, as some of those obtained in the present competitive intermolecular experiments are, may be the outcome of a rate-determining step not related to the C–H(D) bond-cleavage process. This can be true, for instance, for 2-adamantanol assuming that it is produced by rate-determining reduction of a common M–OOC(H)R₂ precursor via O–O cleavage. Importantly, the KIE value for cyclohexanol has been shown to substantially increase in the presence of PPh₃ in the catalytic mixture. Hydrogen abstraction to yield the ketone is expected to be facile, hence KIE values for the ketone are largely influenced by the initial C–H cleavage.

Oxidation of adamantane by I/H₂O₂ (20 equiv) in py/AcOH (10:1) under N₂ affords only traces of 2-(1-adamantyl)pyridine (<0.2%). At 150 equiv of H₂O₂, minor amounts of products are observed: 0.4% (2-adamantanone), 0.3% (2-adamantanol), 0.4% (1-adamantanone), and 0.2% (2-(1-adamantyl)pyridine) (3°/2° = 2.6). The reactions are accompanied by evolution of O₂ (monitored by virtue of an oxygen-sensitive Clark electrode), apparently generated by catalase-type decomposition of H₂O₂. Similar catalytic oxidations with H₂O₂ under O₂ afford minor amounts of oxo products: 2-adamantanone (0.5%) and 1-adamantanol (0.6%) (3°/2° = 3.6). Identical results were obtained by employing the 3/H₂O₂ combination. The analogous oxidation with I/-BuOOH (dry, 20 equiv) affords low yields of 4-(1-adamantyl)pyridine (4.0%) and 2-(1-adamantyl)pyridine (4.7%) anaerobically and minor amounts of oxo products under O₂: 2-adamantanone (0.2%), 2-adamantanol (0.15%), and 1-adamantanol (0.5%) (3°/2° = 4.6). Catalytic oxidation with peracetic acid affords only traces of products. Apparently, none of these oxo donors provide viable alternatives to the Zn₃O₂ system. The catalase-type reaction has been noted by the Barton group in conjunction with catalytic reactions mediated by the FeCl₃/H₂O₂ system in the absence of PAH in neat pyridine and by the present I/H₂O₂ combination in py/AcOH (10:1) in oxidations of cyclohexanes.

Oxidation of isopropene (17.19 mmol) by the I/ZnO₂ combination yields the following oxo products: 2-methyl-2-butanol (0.05 mmol), 3-methyl-2-butanol (0.01 mmol), 3-methyl-2-butanone (0.17 mmol), 3-methyl-1-butanol (0.01 mmol), isovaleraldehyde (0.04 mmol), 2-methyl-1-butanol (0.03 mmol), and 2-methylbutyaldehyde (0.08 mmol). The normalized 3°/2°* preference of 3.6/5.1 indicates a net preponderance for the oxygenation of the secondary position and a small, but not negligible, activation of the primary C–H bonds. Oxidation of 2-methyl-1-butanol and 3-methyl-1-butanol under similar conditions affords only traces of the corresponding aldehydes. Oxidation of isopropene by sMMO from M. trichosporium OB3b has been carefully studied to reveal exclusive formation of isopentanols. The product distribution indicates that there is a net preference for the production of tertiary alcohol in the absence of regulatory component B, but that primary alcohols are strongly favored in oxidations with the fully reconstituted enzyme.

Oxidation of pyridine (33.4 mmol) in the absence of other substrates by the system I/ZnO₂ in py/AcOH (10:1) yields 2-HOpy (0.11 mmol), 3-HOpy (0.07 mmol) and 4-HOpy (0.01 mmol), as quantified by ¹H NMR. In addition, 2,2’-bipy (0.01 mmol) and 2,4’-bipy (0.05 mmol) have been detected and evaluated by GC. Reportedly, pyridine (33 mL) is oxidized by FeCl₃ (1 mmol)/PAH (4 mmol)/H₂O₂ (4 mmol) to afford 2-HOpy (1.04 mmol) and 3-HOpy (0.30 mmol) but only traces of 4-HOpy. The system Fe(PA)₃ (10 mM)/H₂O₂ (10 mM) in py/AcOH (2:1) yields 3-HOpy as the primary product. In contrast, we note that HO* addition to pyridine in pulse radiolysis experiments affects 2-HOpy* and 4-HOpy* (2°/1°). Finally, hydroxyl radicals, generated by photolysis of N-hydroxy-2-thiopyridinone in py/AcOH, have been reported to yield hydroxylation products 2-HOpy/3-HOpy/4-HOpy in a ratio of 13.0/1.0/5.9.

The Nature of Active Oxidant(s) in Gift-Type Chemistry.

The most unresolved issue in conjunction with Gift-type oxidations concerns the active oxidant involved. In principle, for O₂- or H₂O₂-based oxidations, this could be a high-valent iron–oxo unit and/or hydroxyl radicals. Structural evidence presented in this investigation reinforces the argument that there exist

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(75) Barton, D. H. R. Personal communication.
ferrous sites in Gif-type solutions which bear intriguing similarities to the diiron site in H$_3$O$_2$ of sMMO. As demonstrated in the structural features of 4, the documented lability of pyridine favors oxygen-rich ligation by acetato moieties which, in turn, may better precondition the diferrous site for dioxygen activation. Indeed, on a qualitative basis compound 4 reacts with dioxygen much more readily than species 3. The relative importance of oxygen- versus nitrogen-rich ligation has been noted in conjunction with structural and functional features of the diiron center in hemerythrin$^{60}$ (oxygen carrier in a nitrogen-rich environment) and sMMO$^{6a,b}$ (oxygen activator in an oxygen-rich environment). Interestingly, products of autoxidation include “as isolated” dfferic species such as [Fe$_2$ZnO$_2$(O$_2$CCH$_3$)$_6$(py)$_3$]$_2^+$ (3) which exhibit more than one analogies with the corresponding diferrous sites in H$_3$O$_2$ of sMMO. Of greater significance, however, would be to characterize the precursor intermediates generated by the interaction of the ferrous sites with dioxygen as suggested by preliminary UV–vis spectra.

The importance of structural parameters to guide further analysis of metal-centered events notwithstanding, functional characteristics are more relevant to the mode of action of the active oxidant involved and potentially revealing with respect to its nature. The product profiles and intermolecular KIE values obtained from Gif-type oxidations in the present study share aspects of, but are not completely consistent with, oxidations performed by genuine hydroxyl radicals (generated by pulse radiolysis)$^{72}$ or high-valent iron–oxyo species, as the latter have been known from studies involving P-450 isozymes/([O 2 CCH 3 ]$_6$(py)$_3$)$_2^+$ which exhibit more than one analogies with the corresponding diferrous sites in H$_3$O$_2$ of sMMO. Of greater significance, however, would be to characterize the precursor intermediates generated by the interaction of the ferrous sites with dioxygen as suggested by preliminary UV–vis spectra.

It can be argued that the enhanced preference for the activation of the secondary positions of adamantane by comparison to typical radical reactions is nevertheless compatible with the action of the most indiscriminate radicals, including HO$^\bullet$ (3$^\circ$2$^\circ$ $\approx$ 2–2.5)$^{72}$. On the other hand, isopentane and other substrates (methylcyclohexane, methylcyclopentane, trans-decalin, 3-ethylpentane, 1,4-trans-dimethylcyclohexane$^{83}$) show a net preference for the oxygenation of the secondary position, a result that needs to be confirmed with a wider selection of substrates. However, the following observations make the presence of free hydroxyl radicals at the sole active oxidant improbable: (i) alcohols (2-adamantanol, isopentanols) are oxidized to the corresponding aldehydes and ketones only to a limited extent; indeed, alcohols are inferior substrates by comparison to the parent alkanes; (ii) toluene is mostly oxidized at the alkyl substituent rather than via addition to the aromatic ring, albeit at low conversions; (iii) products of pyridine oxidation by the present system are not consistent with those obtained from hydroxyl radical oxidations; and (iv) reported$^{22}$ primary positions remain largely unaffected under Gif-type conditions, although the present results with isopentane call for a wider evaluation of the oxygenation at primary sites. The low conversions of benzene to phenol cannot be fully assessed, but do not exclude the presence of low fluxes of hydroxyl radicals, unless the active oxidant is capable of activating the aromatic ring. The fact that hydrogen peroxide, a reagent that may have a higher propensity to generate hydroxyl radicals, does not initiate a viable shunt pathway may also speak against a dominant role for HO$^\bullet$ in the present system. The same result can also be interpreted as indicating absence of ferric peroxy units, generated by the interaction of ferrous sites with dioxygen. However, hydrogen peroxide and dioxygen are most likely acting at substantially different iron centers. Indeed, the μ-oxo compound 1 may be better predisposed to mediate catalase-type activity, as judged by structural similarities with the metal site of manganese-containing catalases$^{84}$ and iron-based catalase mimics.$^{85}$ Interestingly, the all-ferric [Fe$_3$O$_2$(O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]$^{4+}$ has been recently shown$^{86}$ to generate the trisperoxo compound [Fe$_3$(O$_2$)(O$_2$CCH$_3$)$_6$]$^{3+}$ upon interaction with H$_2$O$_2$.

Similarly, the potent oxidant in Gif solutions does not display typical characteristics of high-valent iron–oxyo species, as those are commonly invoked in explaining the activity of P-450 and sMMO. However, the absence of model systems bearing genuine (per)ferryl units and the only recently emerging physicochemical characterization of the iron–oxyo moiety in the biological oxygenases poses limitations to the generality of the comparative assessment. Nevertheless, the present system neither mediates epoxidation of olefinic substrates nor does it exhibit analogous chemo- and regioselectivity toward aliphatic hydrocarbons by comparison to the biological oxygenases. Admittedly, the influence of the protein environment in modulating chemo/regioselectivity may superimpose on the intrinsic ability of the putative iron–oxyo moiety to bring about a given transformation. The small 3$^\circ$2$^\circ$ and KIE values calculated in the present study cannot be easily reconciled with an iron–oxyo unit abstracting a hydrogen atom from a C–H bond via a more or less linear transition state, unless its potency is such that resembles the indiscriminate activity of hydroxyl radicals. A side-on C–H approach to a putative Fe=O moiety would be more consistent with the observed values, but the paucity of primary carbons remains problematic in both cases.

Of great interest in this context will be the exploration of the conditions that influence the formation and govern the lifetime of substrate radicals, potentially generated in oxidations mediated by the 1/ZnO$_2$ system.$^{87}$ With the exception of a limited number of substrates (adamantane being one of them), Barton has concluded$^{29}$ (on the basis of extensive radical-scavenging studies applied to the FeCl$_3$/PAH/H$_2$O$_2$ oxidizing system) that Gif-type oxidations do not involve alkyl radicals (concerted C–H activation), unless a putative Fenton-type Fe$_3$O$_2$H$_2$O$_2$ system preponderates. In a study comparing the same Gif system (as well as the one employing rBuOOH) with P-450 and sMMO, Newcomb has suggested$^{18}$ that Gif-type oxidation of diagnostic radical-clock substrates indicates the presence of diffusively free alkyl radicals, as opposed to short-lived (<100 fs) substrate radicals generated by the action of the biological oxygenases. Although these studies do not directly reveal the nature of the active oxidant responsible for hydrogen abstraction, they are nonetheless suggestive of a fundamental difference in the mode of C–H activation by Gif-type systems and their biological counterparts. It remains to be seen whether this difference is solely due to the intrinsic characteristics of the active oxidant involved (including the high-iron content of the native system). (88) (a) Varynin, V. V.; Vagin, A. A.; Melik-Adamyan, V. R.; Grebenco, A. L.; Khangulov, S. V.; Pogodin, A. N.; Andrianova, M. E.; Vainshtein, B. K. Dokl. Akad. Nauk. SSSR 1986, 288, 877–880. (b) Pecoraro, V. L.; Gelasco, A.; Baldwin, M. J. In Mechanistic Bioinorganic Chemistry; Thorp, H. H., Pecoraro, V. L., Eds.; American Chemical Society: Washington, DC, 1995; pp 265–301. (c) Penner-Hahn, J. E. In Manganese Redox Enzymes; Pecoraro, V. L., Ed.; VCH Publishers: New York, 1992; pp 29–

conclusions

The following are the principal findings of this study:

1. Reduction of basic iron or iron/zinc acetates under Gif-type conditions generates a host of mononuclear, oligonuclear, and polymeric chain ferrous and zinc species which are implicated in pyridine-dependent equilibria; the \([\text{Fe}^{II}(\text{O}_2\text{CCCH}_3)_2\text{py}]_4\) interconversion dominates in py/AcOH solutions, although the exact nature of solution is not presently known.

2. Upon exposure to dioxygen or air, the \(\text{Fe}^{II}/\text{Zn}^{II}\) sites eventually regenerate the basic acetate structure \([\text{Fe}^{II}\text{M}^{III}-\text{O}]\).

Supporting Information Available: Mössbauer spectra of \(1\nu\) and \(1\kappa\) sites. 

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