

Experimental Section

General protocol: The 2-deoxythioglycoside (0.1 mmol), alcohol (1.5 equiv), and DTBMP (4.5 equiv) were dissolved in CH_2Cl_2 (1.0 mL) under argon, using light-protected glassware. After the mixture had been stirred for 1.5 h at 23 °C over molecular sieves (4 Å, <5 microns, freshly activated), powdered AgPF_6 (3–4 equiv) was added at 0 °C. When the reaction was complete (0.5–2 h), pyridine (50 equiv) was added, and the mixture was stirred for a further 0.5 h. Filtration (celite pad, diethyl ether/*n*-hexane (1:4)), concentration, and chromatographic purification provided the 2-deoxyglycoside.

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H₂O₂-Dependent Fe-Catalyzed Oxidations: Control of the Active Species**

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In memory of Olivier Kahn

The reaction of ferrous ion with hydroperoxides has been investigated for more than a century (Fenton chemistry), and yet the mechanism has still not been satisfactorily rationalized. The nature of the reactive species has always been a matter of debate, oscillating between hydroxyl or alkoxyl

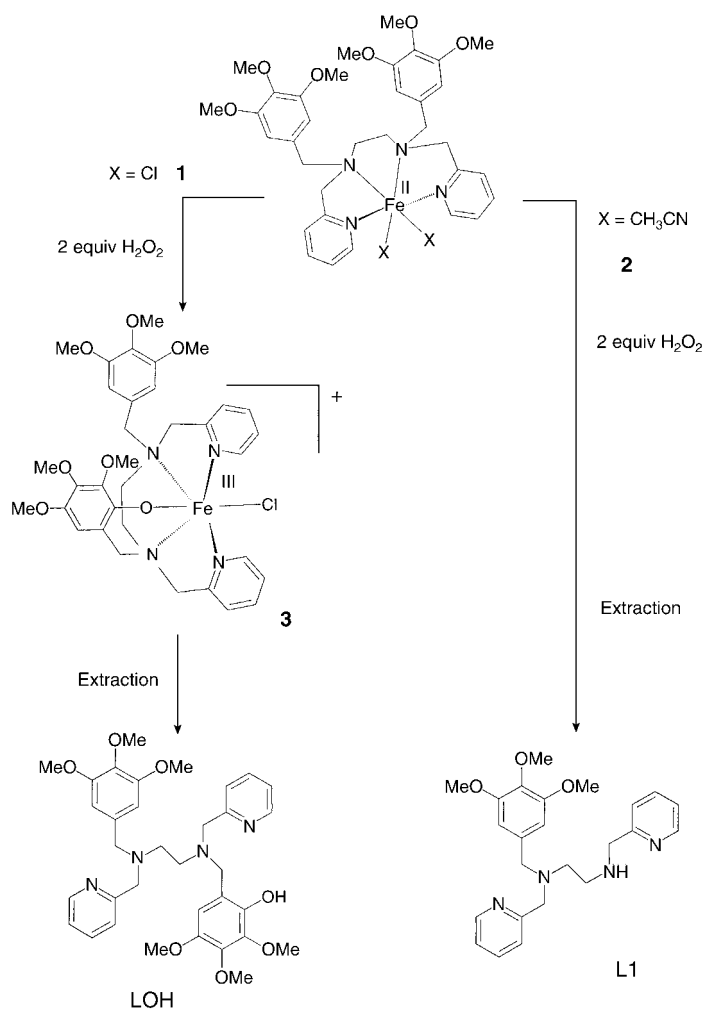
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radicals and an oxene species.^[1,2] Moreover, the discovery that non-heme-iron proteins can oxidize inert substrates (e.g., alkanes) selectively has stimulated chemists to reinvestigate the reaction of non-heme-iron complexes with dioxygen- and oxygen-derived oxidants.^[3] In fact, dinuclear, methane monooxygenase,^[4] and mononuclear non-heme-iron enzymes such as isopenicillin N synthase, 2-oxo-glutarate-dependent enzymes, and pterin-dependent phenylalanine, tyrosine, tryptophan hydroxylases are proposed to carry out a two-electron oxidation via an Fe^{IV} -oxo moiety.^[5] Herein, we report on the oxidation mechanism by using iron complexes of the ligand *N,N'*-bis(pyridin-2-ylmethyl)-*N,N'*-bis(3,4,5-trimethoxybenzyl)ethane-1,2-diamine (L) as a substrate.^[6] This ligand displays several potential oxidation sites, in particular the methylene groups and phenyl rings from benzylic moieties; the latter are known to be very reactive towards hydroxyl radicals, leading to the formation of phenol.^[7] Herein we compare the catalytic properties of two complexes, $[\text{Fe}^{\text{II}}\text{LCl}_2] \cdot 0.25 \text{H}_2\text{O}$ (**1**·0.25 H_2O) and $[\text{Fe}^{\text{II}}\text{L}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2] \cdot 3 \text{H}_2\text{O}$ (**2**(ClO_4)₂·3 H_2O), during oxidation of ligand L (Scheme 1) and of various substrates by H_2O_2 in acetonitrile. With such probes we demonstrate that complex **1** behaves as a typical Fenton reagent, whereas complex **2** functions through metal-based mechanisms. This

shows that for this class of iron complexes the reactivity can be tuned by modifying the simple monodentate ligand.

The synthesis of complexes **1** and **2** started with mixing equimolar amounts of $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ or $\text{Fe}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, respectively, and the ligand L in CH_3OH under argon. Addition of diethyl ether to the CH_3OH solution afforded in both cases a yellow powder. Slow diffusion of diethyl ether into a solution of these powders in acetonitrile afforded crystals suitable for X-ray structure analysis (Figure 1).^[8] The crystal structures of **1**· CH_3CN and **2**(PF_6)₂·2.5 CH_3CN ·0.25 CH_3OH ·0.5 H_2O reveal that in each case the Fe center is octahedrally coordinated; the coordination differs with respect to the nature of the two ligands that occupy the two *cis*-positioned open sites of the Fe^{II} coordination sphere: in compound **1** they are filled by chloride ions, whereas in **2** they are filled by acetonitrile solvent molecules. This difference confers a different spin state to the ferrous ion in the solid state only (shown by the longer Fe–N distances in **1** than in **2**). Complexes **1** and **2** displayed significantly different



Scheme 1. Ligand oxidation of complexes **1** and **2** to give LOH and L1, respectively.

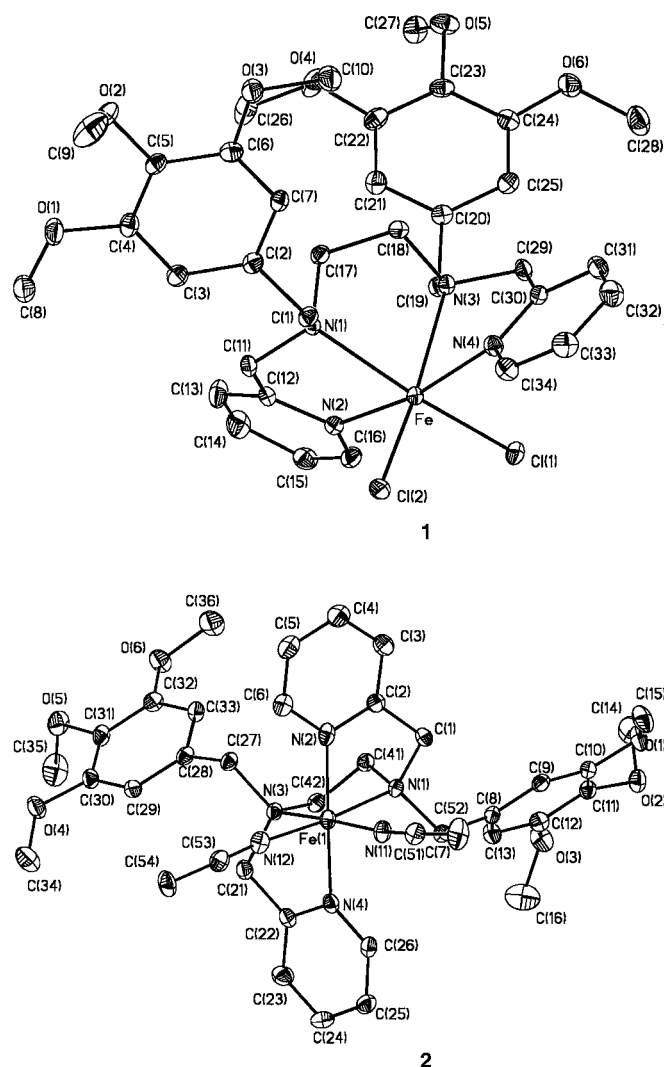


Figure 1. ORTEP representation of complexes **1** and **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$]: for **1**: Fe–N(1) 2.3272(7), Fe–N(2) 2.2120(6), Fe–N(3) 2.3012(6), Fe–N(4) 2.2228(6); for **2**: Fe(1)–N(11) 1.939(4), Fe(1)–N(12) 1.942(4), Fe(1)–N(2) 1.986(4), Fe(1)–N(4) 1.988(4), Fe(1)–N(1) 2.055(4), Fe(1)–N(3) 2.061(4).

resonance signals in their ^1H NMR spectra in acetonitrile between $\delta = 160$ and -20 (data not shown).

When an excess of H_2O_2 was added to a solution of complex **1** (1 mM) in acetonitrile under argon, the solution immediately turned blue. Titration studies showed that only two equivalents of hydrogen peroxide were required to achieve maximal intensity of a new transition at 740 nm. The new species was characterized as a mononuclear phenolatoiron(III) complex $[\text{Fe}^{\text{III}}(\text{LO})\text{Cl}_2]$ (Scheme 1) based on the following spectroscopic signatures: 1) the transition at 740 nm was assigned to a charge-transfer band from an oxygen atom of the phenolato ligand to an iron(III) center;^[9] 2) the positive-ion mode ESI mass spectrum of the resulting solution displayed only one molecular peak at m/z 708 (100%) attributed to $[\text{Fe}(\text{L}-\text{H})\text{Cl} + \text{O}]^+$ whose isotopic pattern was in agreement with the theoretical one; 3) an isotropic signal was observed at $g = 4.3$ in the EPR spectrum of the resulting solution.

The oxidized ligand was then extracted and characterized^[10] by ESI-MS and ^1H NMR analysis as *N*-(2-hydroxy-3,4,5-trimethoxybenzyl)-*N,N'*-bis(pyridin-2-ylmethyl)-*N'*-(3,4,5-trimethoxybenzyl)ethane-1,2-diamine which results from the hydroxylation at the *ortho* position of one phenyl ring of the ligand.^[11] HPLC titration showed that more than 70(± 10)% of the ligand **L** had been transformed into LOH and only 6(± 5)% of the starting ligand was found unconverted.^[12] Mass spectrometric analysis of the modified ligand LOH obtained when $\text{H}_2^{18}\text{O}_2$ was used as an oxidant established that the oxygen atom incorporated came exclusively from the oxidant. Control experiments in the presence of H_2^{16}O in the $\text{H}_2^{18}\text{O}_2$ -dependent reaction did not alter the yield of ^{18}O -atom incorporation. Aromatic hydroxylation of the ligand in iron complexes has been previously reported.^[6, 13]

In contrast, addition of H_2O_2 to complex **2** (ClO_4)₂ under the same conditions as for **1** did not result in any intense color change.^[14] Moreover, extraction of the organic material from the reaction mixture and analysis by HPLC led to the recovery of 65(± 10)% of the unconverted ligand **L** and the isolation of a new modified ligand **L1** in 14(± 5)% yield (see Scheme 1). **L1** was characterized by ESI-MS and ^1H NMR analysis^[15, 16] as *N,N'*-bis(pyridin-2-ylmethyl)-*N*-(3,4,5-trimethoxybenzyl)ethane-1,2-diamine which resulted from an *N*-dealkylation of the **L** ligand. No evidence for the formation of LOH in this reaction was obtained. Clearly, the nature of the two monodentate ligands (Cl vs. CH_3CN) influenced the selectivity of the ligand oxidation, suggesting the participation of different oxidative species.

To distinguish between these reactive species, the catalytic properties of the **1**/ H_2O_2 or **2**/ H_2O_2 combination towards external substrates was studied.^[17] Only **2** led to catalytic and stereoselective alkane hydroxylation under anaerobic conditions. For example, the reaction of *cis*-1,2-dimethylcyclohexane with **2**/ H_2O_2 led to the catalytic formation of *cis*-1,2-dimethylcyclohexanol and *trans*-1,2-dimethylcyclohexanol in a 10:1 ratio (yield based on the oxidant 20%), whereas the analogous reaction with the **1**/ H_2O_2 combination led to an equimolar mixture of *cis*- and *trans*-1,2-dimethylcyclohexanol (yield 7%). Furthermore, catalytic oxidation of cyclohexane to give cyclohexanol and only minor amounts of cyclohex-

anone (yield based on the oxidant 38%; alcohol/ketone 8/1) occurred only with complex **2**, whereas equimolar amounts of alcohol and ketone were detected with complex **1** as the catalyst (yield based on the oxidant 6%). The origin of the oxygen atom incorporated into cyclohexane has been determined in both cases.^[18] When 10 equivalents of $\text{H}_2^{18}\text{O}_2$ were mixed with **2** in the presence of 1000 equivalents of H_2^{16}O , 47(± 3)% of the cyclohexanol was ^{18}O -labeled. This was confirmed when ^{18}O -labeled water and unlabeled H_2O_2 were used. In contrast, with complex **1** and $\text{H}_2^{18}\text{O}_2$, cyclohexanol was fully labeled with the oxygen atom from the oxidant; no exchange with water was observed. Finally, only complex **2** was capable of epoxidizing cyclooctene (30% yield based on the oxidant) and cyclohexene (20% yield based on the oxidant) substrates.^[19] Notably, in the case of cyclohexene, allylic oxidation products were the major products regardless of the catalyst (only 2-cyclohexen-1-ol was formed; yield 10%).

All these data taken together imply two different oxidative pathways depending upon the catalyst structure. In the case of complex **1**, the quasi-quantitative hydroxylation of the pendant phenyl ring of the ligand, the origin of the oxygen atom from the oxidant, the poor (stereo)selectivity during alkane oxidation, and the lack of epoxidation strongly suggest that freely diffusing $\text{OH}^\bullet$ is the active species.^[20, 21] In contrast, in the case of complex **2**, the high stereoselectivity, the solvent oxygen atom exchange, the oxidation of the closest C–H bond of the ligand (the methylene group of the benzyl ring), and the reasonable yield of epoxides can be interpreted with the involvement of an iron–oxo complex as an active species, allowing a better control of the substrate radicals (“caged radicals”) by the metal center. The participation of free hydroxyl radicals when catalyst **2** was used is thus unlikely. The presence of products labeled with oxygen atoms from both water and the oxidant has already been observed in oxidations dependent on heme- and non-heme-iron complexes and has been explained by a postulated “oxo–hydroxo tautomerism” of the Fe^{IV} or $\text{Fe}^{\text{V}}=\text{O}$ intermediate.^[22–25]

One possible explanation for the difference between **1** and **2** is the presence of labile sites only in **2**, which thus allow the binding of H_2O_2 to the metal center. Complex **1** would thus react with H_2O_2 through an outer-sphere electron transfer resulting in formation of $\text{OH}^\bullet$. In contrast, with complex **2** an iron–peroxo species, similar to peroxo complexes previously observed during H_2O_2 -dependent reactions, can be transiently formed as a precursor for a metal-based oxidative species.^[26] The nature of this species remains to be established. We favor a homolytic cleavage of the $\text{FeO}-\text{OH}$ bond, leading to a caged $[\text{Fe}^{\text{IV}}=\text{O} \text{ OH}^\bullet]$ radical pair.

This work further supports the notion that high-valent iron–oxo species (and not only $\text{OH}^\bullet$ radicals) can be generated and used as active species in non-heme-iron catalysis. Furthermore, it shows that the balance between different catalytic pathways for the oxidation ($\text{OH}^\bullet$ vs. metal-based oxidant) can be tuned through the manipulation of the coordination sphere of the ferrous ion.

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- [8] Selected physical data for **1**: Elemental analysis for **1**·0.25H₂O (C₃₄H_{42.5}Cl₂FeN₄O_{6.25}) ($M_r = 733.4$): calcd: C 55.62, H 5.79, N 7.63, Cl 9.68, Fe 7.63; found: C 55.45, H 5.87, N 7.64, Cl 9.75, Fe 7.68; ESI/MS (CH₃CN): m/z : 693 (100%) [FeLCl]⁺; UV/Vis (CH₃CN): $\lambda_{\max}$ (ϵ , m⁻¹cm⁻¹): 415 nm (1050). Crystal data of **1**·CH₃CN: C₃₆H₄₅Cl₂FeN₅O₆, $M_r = 770.52$, triclinic, space group $P\bar{1}$, $a = 13.1459(2)$, $b = 15.5146(2)$, $c = 18.5430(2)$ Å, $\alpha = 92.19(1)$, $\beta = 98.22(1)$, $\gamma = 99.93(1)^\circ$, $V = 3679.34(8)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.391$ g cm⁻³, $\mu = 0.607$ mm⁻¹, $\lambda = 0.71073$ Å, direct methods, $R[I > 2\sigma(I)] = 0.0305$ for 12229 independent reflections of the 17177 collected, $R(\text{all data}) = 0.046$. Selected physical data for **2**: Elemental analysis for **2**(ClO₄)₂·3H₂O (C₃₄H₄₈Cl₂FeN₄O₁₇) ($M_r = 911.3$): calcd: C 44.80, H 5.26, N 6.15, Cl 7.78, Fe 6.15; found: C 44.80, H 5.44, N 6.16, Cl 8.22, Fe 5.75; ESI/MS (CH₃CN): m/z : 757 (100%) [FeLClO₄]⁺; UV/Vis (CH₃CN): $\lambda_{\max}$ (ϵ , m⁻¹cm⁻¹): 377 nm (1700). Suitable crystals for an X-ray analysis were obtained after a metathesis of ClO₄ for PF₆ anions. Crystal data of **2**(PF₆)₂·2.5 CH₃CN·0.25 CH₃OH·0.5 H₂O: C_{43.25}H_{57.5}F₁₂P₂FeN_{8.5}O_{6.75}, $M_r = 1144.22$, triclinic, space group $P\bar{1}$, $a = 13.3988(9)$, $b = 14.5835(9)$, $c = 27.8533(17)$ Å, $\alpha = 98.096(1)$, $\beta = 94.746(1)$, $\gamma = 94.264(1)^\circ$, $V = 5349.4(6)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.421$ g cm⁻³, $\mu = 0.437$ mm⁻¹, $R[I > 2\sigma(I)] = 0.0748$ for 24469 independent reflections of the 34761 collected, $R(\text{all data}) = 0.1708$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146454 (**1**) and CCDC-146455 (**2**(PF₆)₂). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [10] The resulting solution was concentrated and diluted in water in the presence of excess dithionite and bathophenanthroline. The organic material was extracted from the solution by using dichloromethane and chloroform.
- [11] Comparisons between ¹H and ¹³C NMR spectra of **L** and LOH allowed us to unambiguously attribute the inserted oxygen position. In fact, the signal at $\delta = 6.63$ corresponding to the *o*-H for **L** is replaced by two signals at $\delta = 6.63$ and 6.42 in a 2:1 ratio for LOH. A similar trend is observed in the ¹³C NMR spectrum (for the *o*-C of the phenyl ring signals appear at $\delta = 108.5$ and 105.5 for LOH, but only at $\delta = 105.0$ for **L**). ESI-MS for LOH (CH₂Cl₂; positive-ion mode): m/z : 619 (100%) for [LOH + H⁺].
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- [16] Accordingly, the pendant product of the N-dealkylation of the ligand, 3,4,5-trimethoxybenzaldehyde, has been quantitatively detected.
- [17] Experimental conditions: complex/alkane/H₂O₂ 1/1100/10 in acetonitrile inside a glove box (dioxxygen content less than 1 ppm) using syringe pump conditions; delivering time = 30 min [complex] = 0.7 mM.
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A Route to a Germanium–Carbon Triple Bond: First Chemical Evidence for a Germyne**

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Since the isolation of the first disilene, a compound containing a silicon–silicon double bond, in 1981,^[1] many stable compounds with a double bond involving the Group 14 elements Si, Ge, and Sn have been synthesized.^[2] In contrast, compounds containing a triple bond to a Group 14 element other than C remained unknown. Power^[3] described recently a lead analogue of an alkyne (ArPbPbAr) but more consistent with a diplumbylene form. However, some compounds with triple bonds to Si were identified by spectroscopy or by

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