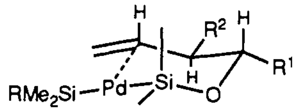
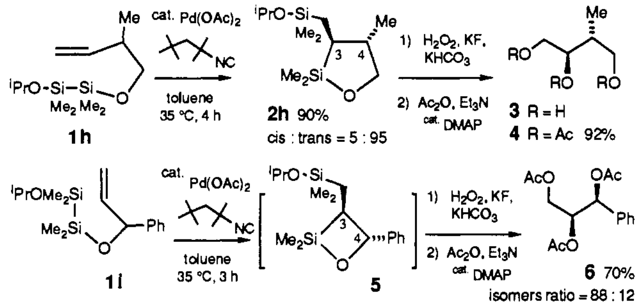
with an enhanced reactivity toward bis-silylation. The present bis-silylation did not require an electron-withdrawing group on the silicon atom (entry 1). Furthermore, a tertiary alkyl-silicon bond was readily formed by the bis-silylation of a geminally disubstituted olefin (entry 7). However, vicinally disubstituted olefins were found not to undergo bis-silylation.

It is noteworthy that bis-silylation of alkenes having an asymmetric center in the tether proceeded with high diastereoselection.[8] Alkenes having allylic substituents, i.e., α to the C=C bond, gave *trans*-**2** (entries 2 and 3), whereas substituents β to the C=C bond favored *cis*-**2** (entries 4-7). The stereoselectivity of the reaction is formulated as arising through a preference for a six-membered cyclic transition state **2t**, in which the substituents R^1 or R^2 are equatorial.



2t

The stereoselective intramolecular bis-silylation of olefinic disilanyl ethers, readily prepared from allylic and homoallylic alcohols, is synthetically useful. Thus, oxidation of the two carbon-silicon bonds of the bis-silylation products introduces two hydroxyl groups leading to the stereo- and regio-defined synthesis of triols as demonstrated in the **1h** to **4** and **1i** to **6** conversions. The use of isopropoxydisilyl ether derivatives of olefinic alcohols facilitates the ultimate oxidation of the silicon-carbon bond. The olefinic disilanyl ether **1h** underwent stereoselective bis-silylation to furnish **2h**, which was oxidized with retention of stereochemistry at carbon[9] to *threo*-3-methylbutane-1,2,4-triol (**3**), a versatile intermediate for the syntheses of δ-multistriatin[10] and ionophore antibiotic X-14547A.[11] Similarly, the olefinic disilanyl ether **1i** was converted to 1,2,3-triol triacetate **6** with moderate stereoselection (88:12) by intramolecular bis-silylation and subsequent oxidation. The stereochemistry of **6** suggests formation of the trans-disubstituted four-membered bis-silylation product **5** analogous to **2a**, although the four-membered silyl ether **5** was too unstable to be isolated and characterized.[12] Thus, intramolecular bis-silylation followed by oxidation offers a new entry to stereoselective dihydroxylation of olefins.



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Supplementary Material Available: Experimental details for the synthesis and identification of **2a-h**, **4**, and **6** (6 pages). Ordering information is given on any current masthead page.

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(8) Details of the assignment of stereochemistry are described in the supplementary material.

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(12) The mixture was oxidized directly to triol after removal of catalyst by filtration through a short column of Florisil.

Models for Non-Heme Iron Oxygenases: A High-Valent Iron-Oxo Intermediate

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The ferryl (Fe=O) species has been demonstrated to be an intermediate in heme peroxidase chemistry[1] and implicated in cytochrome P-450 catalyzed oxygenations.[2] By analogy to these heme enzymes, ferryl species are increasingly being proposed in the mechanisms of dioxygen activation by non-heme iron enzymes[3-6] and invoked in the chemistry of several non-heme alkane functionalization catalysts.[7] Although transient non-heme iron-oxo species have been reported, they have not been fully characterized,[8,9] and the actual viability of an iron(oxo) intermediate in the absence of a porphyrin ligand has yet to be firmly established. During the course of our alkane functionalization studies,[10] we have identified a reactive intermediate derived from the reaction of a (μ-oxo)diferric complex with hydrogen peroxide and report here the spectroscopic characterization of this novel high-valent non-heme iron species.

The reaction of $Fe(ClO_4)_3$ with TPA[11] in the absence of other coordinating anions affords $Fe_2TPA_2O(ClO_4)_4$ (**1**),[12] which has

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(11) Abbreviations used: TPA = tris(2-pyridylmethyl)amine; OAc = acetate; Por = porphyrin.

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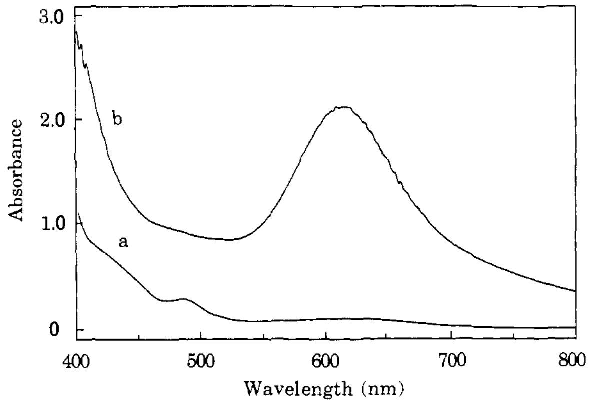

Figure 1. Electronic spectra at −40 °C in CH_3CN (0.1-cm path length) of (a) **1** (6.1 mM) and (b) **1** (6.1 mM) + 1.5 equiv of H_2O_2.

spectral features similar to those of $[Fe_2TPA_2(\mu\text{-}O)\{\mu\text{-}O_2P(OPh)_2\}](ClO_4)_3$.[13] **1** exhibits ^1H NMR isotropic shifts for TPA indicative of strong antiferromagnetic coupling, two Mössbauer doublets at 140 K (ΔE_{Q_1} = 1.57 mm/s, ΔE_{Q_2} = 1.03 mm/s, and $\delta_1 = \delta_2$ = 0.42 mm/s), and a Raman spectrum with ν_s(FeOFe) at 456 cm^{-1}. These features are diagnostic for a bent (μ-oxo)diiron(TPA) complex.[14]

Like other Fe(TPA) complexes,[10] **1** catalyzes the room temperature hydroxylation of cyclohexane in the presence of *t*-BuOOH or H_2O_2.[15] Interestingly, a fleeting green color is observed with H_2O_2 as oxidant. At −40 °C **1** reacts with 1 equiv of 30% H_2O_2 in acetonitrile to form a metastable dark green species (**2**) that persists for over 2 h. The addition of 1 equiv of Ph_3P discharges the color within seconds and results in the stoichiometric formation of Ph_3PO, while the addition of cumene affords a ca. 50% yield of the tertiary alcohol.[16]

Species **2** exhibits a visible spectrum (Figure 1b) with λ_{max} at 614 nm (ϵ = 3500 M^{-1} cm^{-1}). Excitation at 614 nm affords a resonance Raman spectrum with prominent bands at 416 and 666 cm^{-1}, which shift to 408 and 638 cm^{-1}, respectively, upon addition of $H_2{}^{18}O$,[17] but are unaffected by the presence of D_2O. These observations rule out the possibility that **2** is simply a peroxide adduct of **1**, i.e., $[Fe_2TPA_2O(O_2)]^{2+}$.[18] However, the solvent exchangeability and the large ^{18}O shift observed prompt us to assign the 666-cm^{-1} band to an Fe–O stretch ($\Delta\nu_{obsd}$ = −28 cm^{-1}; $\Delta\nu_{calcd}$ = −29 cm^{-1}). For comparison, the ν(M–O) values for oxometalloporphyrin complexes range from 622 to 1025 cm^{-1} and are sensitive to the electronic configuration of the metal center, the basicity of the trans ligand, the nature of the porphyrin and

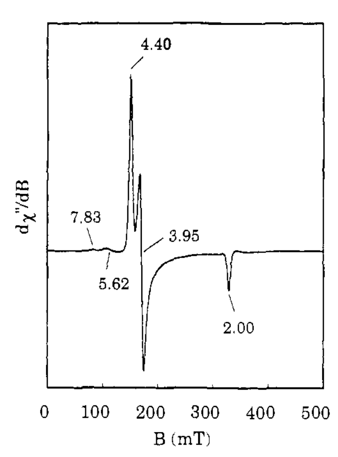

Figure 2. X-band EPR spectrum of **2**, formed from the addition of 1.5 equiv of H_2O_2 to **1** (8.1 mM) at −40 °C in CH_3CN. Experimental conditions: T = 2.1 K, 9.2-GHz microwave frequency, 0.1-mW microwave power, 10-G modulation amplitude, 50 receiver gain. Signals ascribed to **2** quantitate to 0.47 spin/Fe. Features at g = 5.6 and 7.8 are impurities in the starting material and account for <6% of the Fe in the sample.

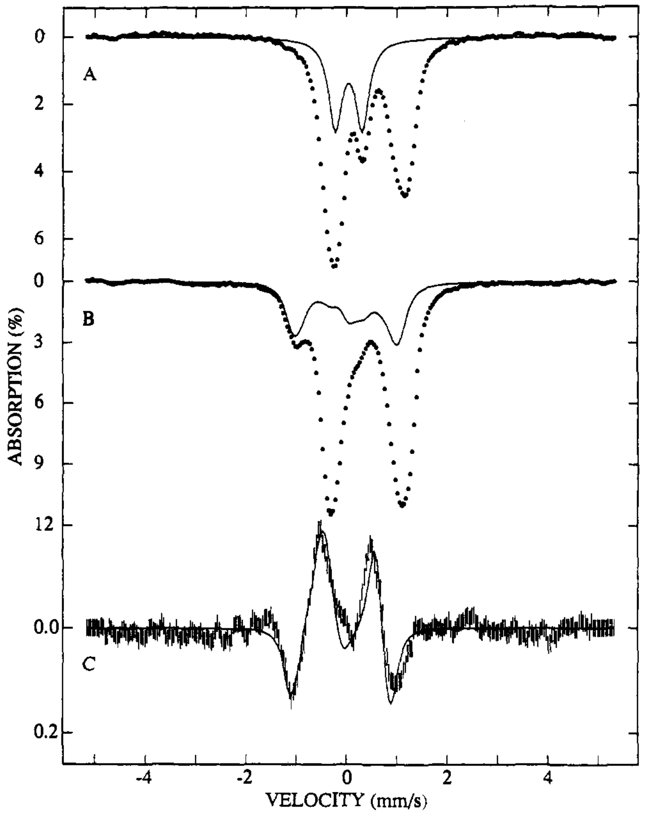

Figure 3. Mössbauer spectra of ^{57}Fe-enriched **1** (2.0 mM) after reaction with 5 equiv of H_2O_2 in CD_3CN at −40 °C. (A) Zero-field spectrum recorded at 140 K. Solid line indicates contribution of **2**. (B) A 4.2 K spectrum recorded in a 0.15-T field applied parallel to the observed γ radiation. (C) A 4.2 K difference spectrum obtained by subtraction of a 60-mT perpendicular-field spectrum from a 60-mT parallel-field spectrum. The solid lines in parts B and C of Figure 3 are theoretical spectra computed from:

$$H = \beta\vec{S}'\cdot\vec{g}\cdot\vec{H} + \vec{S}'\cdot\vec{A}\cdot\vec{I} + \frac{eQV_{zz}}{12}\left[3I_z{}^2 = \frac{15}{4} + \eta(I_x{}^2 - I_y{}^2)\right]$$

with A_x = −16 (3) MHz, A_y = −17 (3) MHz, A_z = −7 (4) MHz, ΔE_Q = 0.53 (4) mm/s, δ = 0.11 (2) mm/s, η = 1, where $S' = {}^1/_2$ is the fictitious spin of the ground doublet.

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(12) $[Fe_2TPA_2(O)](ClO_4)_4$ is synthesized by combination of 0.591 g of TPA·3$HClO_4$ (1.0 mmol) and 4.5 equiv of triethylamine with 0.531 g of $Fe^{III}(ClO_4)_3\cdot10H_2O$ (1.0 mmol) in 20 mL of methanol. A dark green/brown solid precipitates from the solution overnight in 79% yield. Anal. Calcd for $[Fe_2TPA_2(O)](ClO_4)_4$ (**1**) ($C_{36}H_{36}Cl_4Fe_2N_8O_{17}$): C, 39.09; H, 3.28; N, 10.13. Found: C, 38.89; H, 3.38; N, 10.19. UV/vis (CH_3CN, −40 °C): λ (ϵ, mM^{-1} cm^{-1}) 324 (11.0), 430 (sh), 487 (0.5), 612 nm (0.2). ^1H NMR (CD_3CN, −30 °C): δ 34 (br), 26 ppm (br), (19,18,14,13-*m*-pyr), (8,7,6-*p*-pyr). **CAUTION!** Metal perchlorate complexes with organic ligands are potentially explosive. Care should be exercised in handling these compounds, and they should only be prepared in small quantities.

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(15) The reaction of **1** + 150 equiv of *t*-BuOOH or H_2O_2 with 1100 equiv of cyclohexane for 15 min at 25 °C produced cyclohexanol, cyclohexanone, and (*tert*-butyldioxy)cyclohexane. Values of (moles of product)/(moles of catalyst) for *t*-BuOOH are 4, 15, and 22, respectively; those for H_2O_2 are 1, 2, and 0, respectively.

(16) In the absence of **1**, Ph_3P reacts with H_2O_2 under the same conditions to afford 20% oxide, while cumene is unreactive.

(17) The Fe–^{18}O sample was prepared by adding 30% aqueous $H_2{}^{16}O_2$ diluted in $H_2{}^{18}O$ (20:1 $H_2{}^{18}O$:$H_2{}^{16}O$) to a 5 mM sample of **2** in CH_3CN or CD_3CN at −40 °C. The sample was then quickly frozen, and Raman data was acquired at 80 K. No decomposition of the frozen sample was noted after 8 h of irradiation.

(18) The $\nu_{O\text{-}O}$ for peroxide coordinated in any mode is expected to be observed in the 800–900-cm^{-1} region and would not be affected by $H_2{}^{18}O$; for example, see: (a) Ménage, S.; Brennan, B. A.; Juarez-Garcia, C.; Münck, E.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6423–6425. (b) Ahmad, S.; McCallum, J. D.; Shiemke, A. K.; Appelman, E. H.; Loehr, T. M.; Sanders-Loehr, J. *Inorg. Chem.* **1988**, *27*, 2230–2233. (c) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1986; pp 426–433.

its oxidation state, and the presence of hydrogen-bonding interactions.[19] The 416-cm^{-1} feature is tentatively assigned to a metal–ligand vibration coupled to the Fe–O stretch.[20]

Species **2** exhibits an EPR spectrum (Figure 2) with principal **g** values at $g_x = 3.95$, $g_y = 4.40$, and $g_z \sim 2.00$, assigned to the ground Kramers doublet ($S' = {}^1/_2$) of a system with half-integral spin. Its intensity accounts for as much as 0.47 spin/Fe and correlates well with the intensity of the 614-nm band. The EPR spectrum is reminiscent of an $S = {}^3/_2$ multiplet with zero field splitting parameters $D > 0$ and $E/D = 0.04$. The Mössbauer spectra shown in Figure 3 were obtained after treating **1** with 5 equiv of H_2O_2. Approximately 65% of the iron is diamagnetic and consists of two unresolved doublets ($\Delta E_{Q_1} = 1.63$ mm/s, $\Delta E_{Q_2} = 1.15$ mm/s, and $\delta_1 = \delta_2 = 0.44$ mm/s at 140 K). The remainder (ca. 30%) belongs to Kramers species **2**. At 140 K the spectrum of **2** consists of *one* quadrupole doublet (Figure 3a) with $\Delta E_Q = 0.53$ mm/s and $\delta = 0.07$ mm/s. Relative to **1**, the isomer shift of **2** has changed from 0.42 mm/s to 0.07 mm/s, showing that **2** is oxidized relative to **1**, most probably to the Fe(IV) state. In fact, the observed value of δ is similar to those of Fe(IV) complexes in heme[21] and non-heme[22] environments. At 4.2 K, **2** exhibits paramagnetic hyperfine structure (solid line in Figure 3b) as expected for a Kramers species and has a magnetic field dependence (60 mT $\perp$ vs 60 mT $\|$) predictable from the EPR spectrum (solid line in Figure 3c).[23] The EPR spectrum of the Mössbauer sample accounts for 0.3 spin/Fe. Since 30% of the ^{57}Fe Mössbauer absorption is associated with **2**, the EPR and Mössbauer data, taken together, strongly suggest that **2** is a *mononuclear* rather than a dinuclear complex.[24]

The spectroscopic data lead us to postulate the following reaction scheme:

$$\underset{\mathbf{1}}{[\mathrm{LFe{-}O{-}FeL}]^{4+}} + \mathrm{H_2O_2} \rightarrow \underset{\mathbf{2}}{[\mathrm{LFeO}]^{3+}} + \underset{\mathbf{3}}{[\mathrm{LFeOH}]^{2+}} + \mathrm{OH^-}$$

In this scheme, treatment of **1** with H_2O_2 causes the 2e oxidation of one of the ferric ions. Subsequent cleavage of the dinuclear complex yields **2** and ferric complex **3**; the latter then dimerizes to form the spin-coupled diferric complex of parts a and b of Figure 3, which does not react with H_2O_2 at -40 °C. Thus, a stoichiometric formation of **2** would correspond to a maximum of 0.5 spin/Fe. It is clear from the spectroscopic data that **2** is a novel species; it is a Kramers system containing the non-Kramers ion Fe(IV) and exhibits remarkably small magnetic hyperfine interactions. These unusual observations can be reconciled with a model that considers ferromagnetic coupling ($H = JS_1 \cdot S_2$, $J < 0$) of an $S = 1$ ferryl complex[25] ($D > 15$ cm^{-1}, $E/D = 0.04$) to an $S = {}^1/_2$ radical, with coupling strength $J/D \sim -1.5$.[26] We therefore formulate **2** as $[(\mathrm{L}^{\bullet+})\mathrm{Fe^{IV}{=}O}]^{3+}$, a species with electronic features similar to those of heme peroxidase compounds I[1a,27] and related to the putative $[(\mathrm{Por})\mathrm{Fe(O)}]^+$ species in cytochrome P-450.[2] Thus high-valent iron–oxo species may also play a crucial role in the alkane functionalization reactions catalyzed by non-heme iron centers.

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(20) (a) Attempts to fit the 416- and 666-cm^{-1} bands as ν_s and ν_{as}, respectively, of an Fe–O–Fe or related unit were unsuccessful. (b) In the resonance Raman spectrum of hemerythrin, a band at 292 cm^{-1} displaying a 6-cm^{-1} ^{18}O shift has been assigned to an Fe–N(imidazole) stretch coupled to an Fe–O bond; see: Czernuszewicz, R. S.; Sheats, J. E.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 2063-2067 and references therein.

(21) See Table I in the following: Schulz, C. E.; Rutter, R.; Sage, J. T.; Debrunner, P. G.; Hager, L. P. *Biochemistry* **1984**, *23*, 4743-4754.

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(24) Other Mössbauer samples, produced with different H_2O_2 concentrations, give essentially the same spectroscopic results; in all cases, the concentration of **2** obtained from EPR agrees with that obtained from the Mössbauer studies. Thus, the spectroscopic properties of **2** do not depend on the H_2O_2 concentration.

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Distortion toward Bridging Accompanying Hyperconjugation in a Simple Tertiary Alkyl Carbocation

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The 2-methyl-2-butyl (*tert*-pentyl) cation is the smallest tertiary carbocation that affords the possibility of stabilization through C–C hyperconjugation. The cation could adopt structure **1**, in which the C3–C4 bond is aligned parallel with the "vacant" p orbital at C2$^+$, or the planar geometry, **2**, in which C–C hyperconjugation cannot take place. Despite experimental measurement of a variety of properties,[1-6] detailed information concerning the structure of the *tert*-pentyl cation has been completely lacking. The *tert*-pentyl cation has long been assumed to be "classical", and the NMR chemical shifts have been taken as references for carbenium ion behavior.[1-4] This assumption requires significant refinement, as we will demonstrate in this paper through the use of ab initio structures and IGLO (*i*ndividual *g*auge for *l*ocalized molecular *o*rbitals) chemical shift calculations. Specifically, geometrical distortion toward bridging accompanies C–C hyperconjugation and leads to a reduction of about 20 ppm in the

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