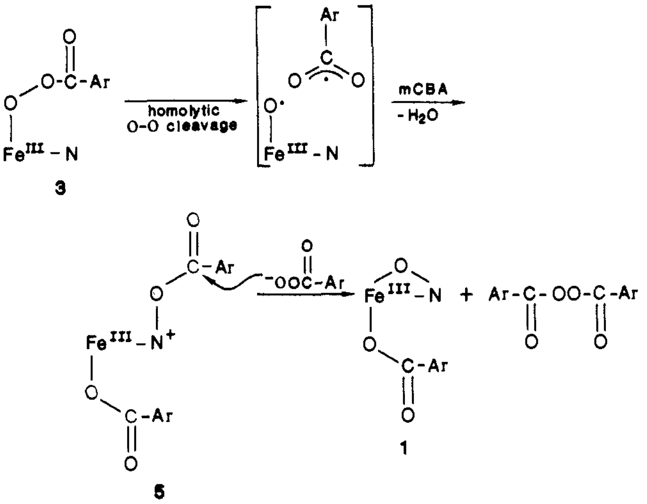
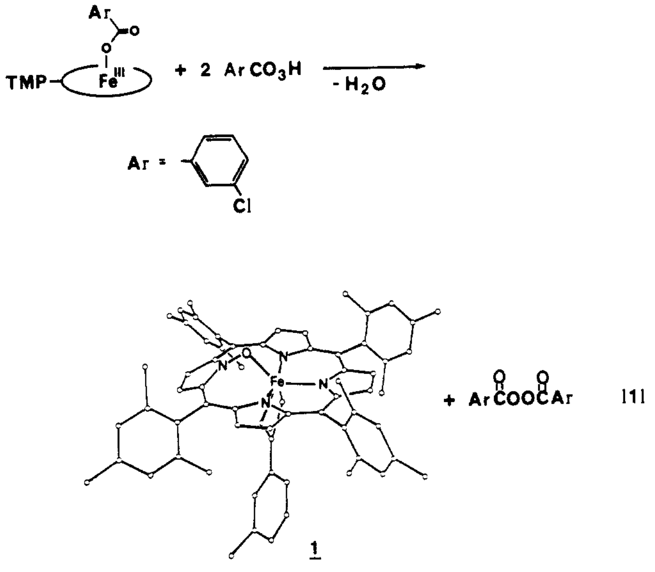
Scheme I



N-bridged iron(III) nitrene[5d] and is consistent with a rhombically distorted high-spin iron(III) electronic configuration for **1**. The solution magnetic susceptibility of **1** determined by the Evans method in toluene-d_8 at −25 °C was found to be 5.4 ± 0.1 μ_B.

Inspection of the FT-IR spectrum in Nujol of the reaction mixture obtained upon addition of mCPBA to Fe^{III}(TMP)(mCB) showed bands for iron-coordinated *m*-chlorobenzoate (1660 cm^{-1}) and prominant peaks for **bis(3-chlorobenzoyl) peroxide** (1796, 1771, 1216, 1012 cm^{-1}). The intensities of these bands indicated that the diacyl peroxide had been produced in amounts equivalent to those of **1**. Additionally, no free *m*-chlorobenzoic acid was evident in the IR spectrum. When this reaction was performed with peroxybenzoic acid, dibenzoyl peroxide could be isolated from the reaction mixture. Accordingly, the stoichiometry for the formation of **1** is as indicated in eq 1.



The reaction of Fe^{III}(TMP)(OH) (10^{-4} M) with mCPBA at −50 °C in toluene showed the immediate formation of Fe^{III}(TMP)(*m*-chloroperoxybenzoate)[9] (**3**) and then a relatively slow decomposition to **1**. The oxidation of Fe^{III}(TMP)(OH) with phenylperoxyacetic acid under these conditions produced (O)=Fe^{IV}(TMP)[1] instead of **1**.[10] At higher concentrations or under more acidic conditions, the mCPBA oxidation of Fe^{III}(TMP)(OH) afforded the oxoiron(IV) porphyin cation radical species **4**,[2a] also via **3**. These observations indicate that there are two modes of iron(III)-mediated O–O bond cleavage. The stoichiometry of the formation of **1**, the concommitant formation of diacyl peroxide, and the decarboxylation of phenylperoxyacetic acid suggest a homolytic process leading to **1** as outlined in Scheme I. The intermediate *N*-(benzoyloxy) iron(III) porphyrin species **5** would be expected to be a good acylating agent, affording **1** and the diacyl peroxide in equimolar amounts. In the preceding paper we describe the acid-catalyzed heterolysis of the O–O bond in **3** to give **4**.[9,11]

That **1** and **4** should both result from **3** indicates that mechanistic implications derived from catalytic reactions must be interpreted with great care. Further, that **1** and **4** are independently isolable compounds suggests that while **4** is still the preferred model for highly oxidizing species in cytochrome P-450 and horse radish peroxidase, iron(III) *N*-oxides such as **1** must be considered for other systems, particularly those in which ligand stabilization of the iron(IV) oxo group may be absent.

Acknowledgment. Support of this research by the National Institutes of Health (GM 36298) and the National Science Foundation is gratefully acknowledged. EPR spectra were obtained by T. P. Radhakrishnan.

Registry No. **1**, 104463-56-1; **2**, 104439-49-8; **3**, 104463-57-2; **4**, 99688-03-6; Fe^{III}(TMP)(mCB), 104463-55-0; H$_2$TMP, 56396-12-4; Fe^{III}(TMP)(OH), 77439-20-4; (O)Fe^{IV}(TMP), 93085-16-6.

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[9] (a) Groves, J. T.; Watanabe, Y., presented in part at the International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 16–21, 1984. (b) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.*, preceding paper in this issue.

[10] GC analysis indicated 63% toluene, 19% benzyl alcohol, and 11% benzyaldehyde base on phenyl peroxyacetic acid.

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Characterization of Transition-Metal Molecular Hydrogen Complexes by Solid-State Proton NMR

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Received June 19, 1986

Recently it has been discovered that stable transition-metal complexes containing molecular hydrogen as a ligand can be prepared.[1] Current research under way in several laboratories[2-9] indicates that the η^2 mode of binding hydrogen is fairly common and even occurs in several polyhydrides previously believed to be classical in structure. These molecules have been cited as examples of an arrested oxidative addition of hydrogen to a metal complex, and the observed variations in physical properties seems to indicate that the addition is halted at different points. Characterization

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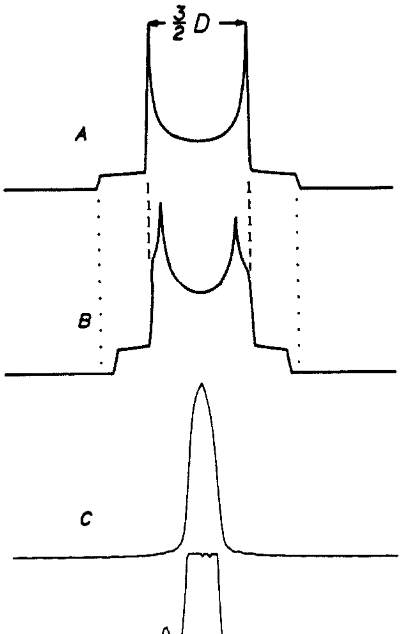

Figure 1. (A) Classical Pake pattern line shape with discontinuities split by 3D/2 and 3D. (B) As modified by a torsional oscillation about an axis perpendicular to the internuclear vector. The outermost discontinuities move closer as do the peaks in the pattern. One set of breaks remains separated by 3D/2. The chemical shift anisotropy produces the asymmetry of the pattern about the midpoint. (C) Experimental solid-state proton spectrum for H_2–$W(CO)_3(PCy_3)_2$ without suppression of the ligand signal. Proton resonant frequency = 300.1 MHz, $\pi/2$ pulse = 0.9 μs, τ = 5μs. (D) Same as (C) but using the ligand suppression sequence with an 8-ms prepulse 100 times weaker than the $\pi/2$ pulses. (E) Same as (D) but for a sample with 95% perdeuterated PCy_3 ligands. The L line has been cut off for clarity. In both cases the line is a factor of 2 larger than the cutoff.

of these η^2-dihydrogen complexes has relied on solution NMR or single-crystal diffraction studies to verify that the H_2 ligand remains intact when bound.[1-7] Interpretation of solution NMR results is complicated by the fluxional nature of these species, and location of the hydrogens by diffraction is hampered by anisotropic motion and disorder of the H_2 ligand.[1] In this paper we report on a simple, generally applicable solid-state NMR method that is well suited for characterizing these species. The method uses the large dipolar couplings between the H_2 protons to determine their separation and does not require single crystals or deuteration of the other coordinating ligands.

The basic principle of the method is not new. Isolated pairs of nuclei in a rigid solid experience a mutual dipolar interaction directly proportional to the average of the inverse cube of the internuclear distance.[10] For a powder sample this results in the familiar Pake doublet line shape[11] indicated in Figure 1A. From a simulation of the line shape the internuclear distance can typically be determined to within 1%.[12,13] Pake patterns are also quite sensitive to the nature of any anisotropic motion.[14,15] For H_2 complexes one might expect a hindered rotation or torsion of the sidebound H_2 about the coordination axis. This motion will not effect the H_2 dipolar splitting when this axis is parallel to the applied magnetic field. One discontinuity in the Pake pattern is then unaffected, giving a precise measure of the H–H distance. The other breaks in the pattern shift as in Figure 1B and from the temperature dependence of the shifts the amplitude and thermal parameters of the motion can be determined.

In most of the known dihydrogen complexes the H_2 ligand is only a few percent of the total proton signal. The other coordinating ligands L generally will give a structureless Gaussian line obscuring the H_2 spectrum. The result in Figure 1C for H_2–W-$(CO)_3(PCy_3)_2$ is a spectrum with no features that can be attributed to the H_2. This problem can be overcome by realizing that since the H_2 essentially experiences only one large dipolar coupling, its line shape is inhomogeneously broadened.[16] A soft pulse then can saturate a small slice in this pattern and not effect the majority of the line shape. The L line on the other hand is homogeneously broadened by the large number of dipolar couplings that these protons experience.[14] A selective pulse therefore cannot burn a hole in the L line and it will be saturated even though the weak pulse is not strong enough to cover the L lines full width. Thus by using a weak pulse prior to a $\pi/2x$–τ–$\pi/2y$–τ dipolar echo,[14] the L contribution to the proton spectrum can be suppressed as shown in Figure 1D. For comparison, a spectrum using the prepulse on a sample prepared with 95% perdeuterated PCy_3 is included in Figure 1E. The suppression of the L signal by the pulse sequence alone is nearly as effective as with isotopic substitution. In cases where scrambling between the H_2 and the other ligands occurs, deuteration will wash out the H_2 signal and the ligand suppression sequence should be used instead.

The spectra in Figure 1D,E display the line shape shown in Figure 1B as expected for a hindered rotation about the coordination axis. The frequency difference between the discontinuities spaced by $3D/2 = 3\gamma^2 h/8\pi^2 r^3$ is $25_6 \pm 5$ kHz, independent of temperature from 80 to 300 K. The complete details of the temperature dependence are complicated and for the present discussion it is sufficient to note that the temperature independence of the one pair of discontinuities rules out thermally activated motion of the H_2 out of the plane of the rotation on the NMR time scale. This splitting gives an apparent H–H distance of 0.890 ± 0.006 Å. Variations of hundredths of an angstrom in the H–H distance would result in easily observable spectral shifts of tens of kilohertz. Thus this method should be useful for following changes in the H–H distance with different coordinating ligands or metal centers. To fully account for the observed line shape the chemical shift anisotropy for the H_2 must also be included.[13] A fit of the line shape gives $\sigma_{11} = 11$, $\sigma_{22} = -5$, and $\sigma_{33} = -6$ ppm relative to the isotropic shift and places[13] σ_{22} along the H–H axis and σ_{33} along the axis of rotation.

To compare the distances measured by NMR and diffraction the averaging effects of other motions must also be considered. The low-temperature behavior of the NMR spectrum indicates that the amplitude of the in plane zero point torsion is $\sim\pm 16°$ and any out of plane zero point motion is expected to be less than this. If the amplitude of the out of plane motion is as great as ±6° the correct internuclear distance would be 0.880 Å. Vibration can likewise result in a larger than expected dipolar coupling; however, these corrections are calculated to be much smaller. Thus even given the uncertainty that zero point motion introduces, the measured equilibrium H–H distance is a very good upper limit with an estimated error of no more than 0.01 Å. Although qualitative, the available data indicate that there is a correlation between the strength of the H_2–M bond and the lengthening of the H–H bond. In order of increasing thermal stability toward loss of H_2 the H–H distances are 0.82 Å for H_2–$W(CO)_3$(P(*i*-

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Pr)$_3$)$_2$ by neutron diffraction,[17] 0.890 Å for H_2-W(CO)$_3$(PCy$_3$)$_2$ reported here by NMR, and 0.89 Å for *trans*-[Fe(η^2-H_2)(H)-(dppe)$_2$]BF$_4$ by X-ray.[3] The latter distance is likely to be in error on the low side as X-ray diffraction will tend to underestimate the distance between the nuclei. A systematic study is currently under way to quantitate this trend by the solid-state NMR method described here. In conclusion dynamic solid-state NMR studies as described here should prove to be a powerful tool for studying the structure and fluxional behavior of this interesting class of compounds.

Acknowledgment. This work was supported by a Camille and Henry Dreyfus Foundation grant for newly appointed young faculty in chemistry. Stimulating discussions with Prof. R. H. Crabtree and Dr. J. M. Millar are gratefully acknowledged. G.J.K. is supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. H_2-W(CO)$_3$(PCy$_3$)$_2$, 104198-75-6.

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Multiple Pathways in the Oxidation of *cis*-Stilbene by Fe-Bleomycin

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Received July 14, 1986

The bleomycins are clinically useful glycopeptide-derived antitumor antibiotics.[2] Their therapeutic effects are believed to derive from their ability to cleave DNA, an oxidative process that can be mediated in vitro by $\mathrm{Fe^{III}}\cdot$BLM + an oxidant (e.g., C_6H_5IO or H_2O_2)[3] or $\mathrm{Fe^{II}}\cdot$BLM + O_2.[4] Bleomycin derivatives so activated have also been shown to effect the oxygenation of olefinic substrates.[3b,5] While the products of BLM-mediated oxidation of DNA and olefins have been characterized, their mechanism(s) of formation are less well-defined. Presently, we provide evidence that oxygenation of *cis*-stilbene by activated Fe·BLM involves at least two oxidative mechanisms.

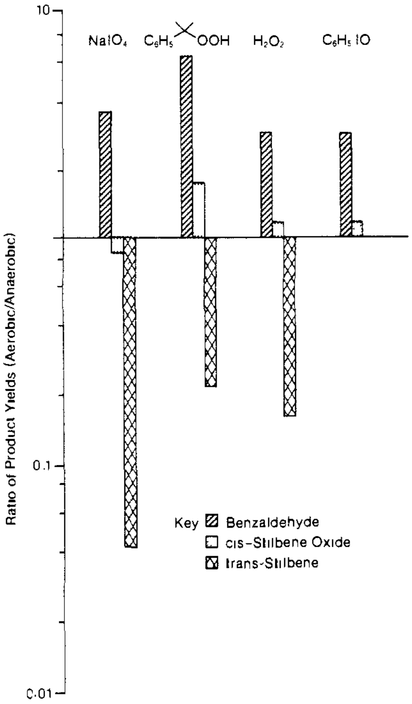

Figure 1. Ratio of aerobic/anaerobic product yields. Values represent the ratios of mean product yields obtained under air vs. under argon[6] and were determined from at least five independent trials with each oxidant under each atmosphere. *trans*-Stilbene formation with C_6H_5IO was found to be BLM-independent; the ratio was therefore omitted.

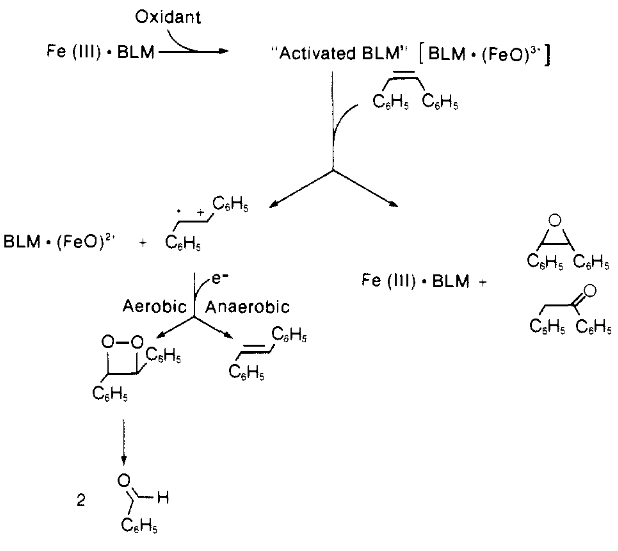

Figure 2. Multiple pathways postulated for *cis*-stilbene oxidation.

Under aerobic conditions, the oxidation of *cis*-stilbene by $\mathrm{Fe^{III}}\cdot$BLM + an oxidant[6] yielded a variety of oxidation products including *cis*-stilbene oxide and benzaldehyde.[5] Exclusion of dioxygen had little effect on the production of *cis*-stilbene oxide, in accord with the hypothesis that O_2 plays no direct role in the formation of this product in exogenous oxidant-supported reactions.[5b] In contrast, in all cases the yield of benzaldehyde was

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[6] Oxidants employed included H_2O_2, NaIO$_4$, C_6H_5IO, and cumene hydroperoxide. In a typical experiment, 15 μL of an aqueous solution of preformed 9.1 mM $\mathrm{Fe^{III}}\cdot$BLM was added to a solution composed of 150 μL of 100 mM *cis*-stilbene in methanol and 285 μL of 8:2 methanol/water. In aerobic experiments, the reaction was initiated by the addition of 50 μL of a 40 mM solution of the oxidant in 8:2 methanol/water. In anaerobic experiments, the oxidant was placed in the top section of a Thunberg tube, with the $\mathrm{Fe^{III}}\cdot$BLM + *cis*-stilbene solution in the bottom section. The tube was then degassed by three vacuum/argon cycles before mixing. Reactions were typically run for 30 min at 37 °C and diluted with 2 mL of aqueous 0.5% NaCl and the products extracted into CH_2Cl_2. Products were quantitated by gas chromatography, using *m*-tolualdehyde and benzophenone as internal standards.

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