$Pr)_3)_2$ 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*-$[Fe(\eta^2\text{-}H_2)(H)(dppe)_2]BF_4$ 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.

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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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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 Fe^{III}·BLM + an oxidant (e.g., C_6H_5IO or H_2O_2)[3] or Fe^{II}·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.

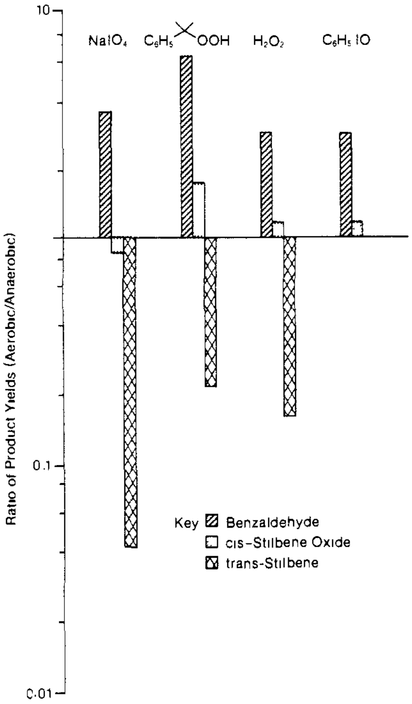

Figure 1. Ratio of aerobic/anaerobic product yields. Values represent the ratios of mean product yields obtained under air vs. under argon[6] and were determined from at least five independent trials with each oxidant under each atmosphere. *trans*-Stilbene formation with C_6H_5IO was found to be BLM-independent;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

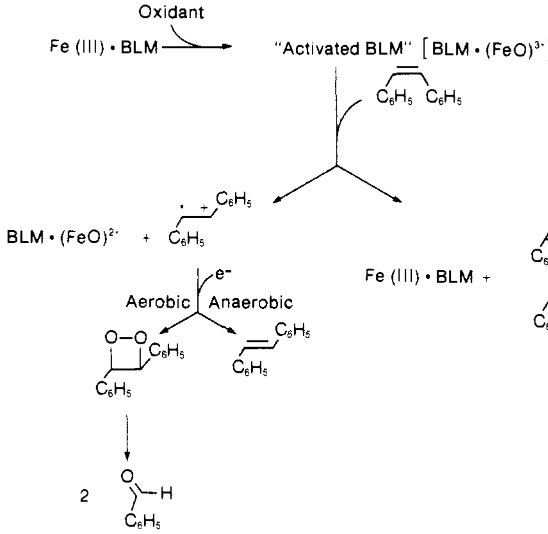

Figure 2. Multiple pathways postulated for *cis*-stilbene oxidation.

Under aerobic conditions, the oxidation of *cis*-stilbene by Fe^{III}·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 Fe^{III}·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 Fe^{III}·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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much lower in the absence of O_2 (Figure 1), and $^{18}O_2$-labeling experiments confirmed that the oxygen atom in the formed C_6H_5CHO was derived predominantly (>60%) from O_2 for three of the oxidants employed. Also detected by gas chromatographic analysis as a product of *cis*-stilbene treatment with activated Fe·BLM was *trans*-stilbene. While formed only to a limited extent in the presence of O_2, *trans*-stilbene was the major product with each oxidant under anaerobic conditions (Figure 1).

That benzaldehyde formation was favored under aerobic conditions, while *trans*-stilbene was formed primarily under anaerobic conditions, suggested that these two products might be derived from a single intermediate that partitioned down one of two pathways depending on the presence or absence of O_2. One candidate for this intermediate is the stilbene cation radical, which could react with O_2 to form benzaldehyde via a dioxetane intermediate or, in the absence of O_2, isomerize to the more stable trans configuration and undergo reduction to *trans*-stilbene (Figure 2). It is of interest that photoexcited dyes catalyzed similar chemistry from *cis*-stilbene, with the same O_2 dependence.[7] In contrast, BLM-mediated stilbene epoxidation was O_2 independent and occurred without loss of stereochemistry. The cis-epoxide is apparently formed via a completely different reaction pathway, which may more closely resemble the monooxygenase chemistry of cytochrome P-450.[5b,8]

Three additional experiments provide support for the scheme outlined in Figure 2. First, the finding that the ratio of C_6H_5CHO to *cis*-stilbene oxide formed under aerobic conditions was essentially constant over the time course (5–30 s) of the H_2O_2-supported reaction was consistent with the formation of both from either a single "activated BLM" intermediate or from two different metal–oxygen species which are kinetically indistinguishable on this time scale. The second finding involved the oxidation of *p*-nitro-*cis*-stilbene under aerobic conditions by Fe^{III}·BLM + H_2O_2. Consistent with the scheme outlined in Figure 2, the ratio of (*p*-nitro)benzaldehyde/(*p*-nitro)-*cis*-stilbene oxide formed was 0.95 for *cis*-stilbene and 0.27 for *p*-nitro-*cis*-stilbene, in parallel with the redox potentials for the two olefins (+1.54 V for *cis*-stilbene; +1.71 V for *p*-nitro-*cis*-stilbene).

While the foregoing results are consistent with the scheme in Figure 2, they do not exclude the possible intermediacy of a stilbene radical; this could form by initial H$^\bullet$ abstraction in analogy with BLM-mediated DNA oxidation.[9] Accordingly, the oxidation of *cis*-stilbene was carried out in D_2O/CD_3OD to test this possible mechanism. When activated in deuterated solvent with any of the oxidants in Figure 1, Fe^{III}·BLM catalyzed the conversion of *cis*-stilbene to *trans*-stilbene with no detectable (<1%) deuterium incorporation. While this finding does not exclude a radical intermediate,[10] given the reactivity of the stilbene intermediate toward O_2, and the proposals that many cytochrome P-450-catalyzed reactions proceed via initial electron abstraction,[8b] the data seem most consistent with the model outlined in Figure 2 and constitute a third line of support.

The nature of the metal–oxo species responsible for the products documented here is uncertain. The similarity in results with each of the oxidants employed suggests, however, that the same intermediate or intermediates are being formed with each oxidant. It is clearly of interest to determine whether the electron abstraction pathway suggested for *cis*-stilbene oxidation is applicable to the Fe·BLM-mediated oxidation of alkenes in vivo.[11]

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[10] It is possible that the stilbene radical intermediate might collapse with H$^\bullet$ abstraction from Fe·BLM. However, the observation that the stilbene intermediate reacts with O_2 in solution, and not with the oxygen of the activated Fe·BLM, suggests that it diffuses away from the BLM "active site" before reacting with O_2.

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Binuclear Platinum(III) Complexes. Preparation, Structure, and dσ → dσ^* Spectrum of $[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(CH_3CN)_2]$

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An intense dσ → dσ^* absorption system is the electronic spectroscopic signature of a d^7–d^7 binuclear complex containing a metal–metal single bond.[2,3] Previous theoretical and experimental work has indicated[2-6] that the highest occupied σ orbital may acquire appreciable axial-ligand character, and, at least in the $[Pt_2(P_2O_5H_2)_4X_2]^{n-}$ (X = axial ligand) series,[4,5] the absorption band positions depend so strongly on X that it has not been possible to assign a dσ → dσ^* energy to the Pt–Pt bond itself. We have addressed this problem in the latter series by utilizing CH_3CN as the axial ligand, because its very stable σ(N) donor orbital should not significantly contaminate the highest occupied dσ Pt–Pt level. Thus the structure and the electronic spectrum of $[Pt_2(P_2O_5H_2)_4(CH_3CN)_2]^{2-}$ should serve as benchmarks in attempts to elucidate axial σ interactions in binuclear platinum(III) complexes.

Dropwise addition of H_2O_2 (30%, 2 mL) to an acetonitrile solution of $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ (0.3 g in 50 mL) containing excess PhSSPh (1 g) yielded a bright yellow solution. Upon addition of diethyl ether, a yellow solid precipitated (> 70% yield). Recrystallization of the crude yellow solid by slow diffusion of diethyl ether into acetonitrile solution gave orange prismatic $[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(CH_3CN)_2]$ crystals together with some starting material.

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