The role of this oxoruthenium(IV) complex in the catalytic olefin oxygenation we have observed with **3** is under continued study. Initial results have indicated that $Ru^{IV}TMP(O)$ is formed from **3** under these conditions but that the rate of disproportionation depends upon the olefin concentration. Finally, it should be noted that $Ru^{IV}TMP(O)$ and related complexes may provide an opportunity to prepare stable model compounds for the biologically important oxoiron(IV) porphyrins.[7,12]

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Registry No. **1**, 97877-74-2; **2**, 110613-27-9; **3**, 92669-44-8; Ph_3P, 603-35-0; ^{18}O, 14797-71-8; $RuTMP(PPh_3)$, 110613-28-0.

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Reactivity of the Triplet State of the Tetrakis(μ-pyrophosphito)diplatinate(II) Tetraanion with Alkenes and Alkynes. Comparison with the Energy-Transfer Photosensitizer and Diradical Chemistry of Ketone Triplets

Sir:

The triplet excited state of the tetrakis(μ-pyrophosphito)diplatinate(II) tetraanion $Pt_2(pop)_4^{4-*}$ continues to show interesting chemistry. This $^3A_{2u}$ state can react as either an oxidant or a reductant toward added reagents,[1] as well as showing the atom-transfer chemistry expected of a triplet state having an odd electron in a $\sigma^*(d_z2)$ frontier orbital.[2] The respective potentials ($E^{\circ\prime}$ vs SCE) for the oxidation and reduction of $Pt_2(pop)_4^{4-*}$ are >1.5 and 1.1 V.[3] On the basis of quenching studies, it has been estimated that this triplet state will abstract hydrogen atoms from C-H bonds that have enthalpies of up to 90 kcal mol^{-1}.[4] The excited state can also be quenched by energy transfer to $Ru(bpy)_3^{2+}$ and condensed aromatics.[5] We now find that alkenes and alkynes will quench the $^3A_{2u}$ state of $Pt_2(pop)_4^{4-*}$ by an energy transfer, a hydrogen atom abstraction, or a diradical mechanism and that the rates and quenching mechanisms can be usefully compared with those found for benzophenone or other ketone triplets.[6]

Table I. Rate Constants for the Reaction of the $^3A_{2u}$ State of $Pt_2(pop)_4^{4-*}$ with Alkenes and Alkynes

alkene	solvent[a]	log k_q[b]
tetramethylethylene	MeOH	0
maleic acid	H_2O	4.0
trans-3-hexene	MeOH	4.6
cyclooctene	MeOH	5.6
1,1-diphenylethylene	MeOH	5.7
1,5-cyclooctadiene	MeOH	6.0
cyclohexene	MeOH	6.1
ethyl vinyl ether	MeOH	6.3
2-hexene	MeOH	6.6
4-pentenol	DMF	6.7
styrene	MeOH	6.8
2,5-dimethyl-3-hexyne-2,5-diol	H_2O	7.0
1,5-hexadiene	DMF	7.2
cis-stilbene	MeOH	7.2
acetylenedicarboxylic acid	H_2O	7.2
1-hexyne	MeOH	7.3
1-hexene	MeOH	7.4
1-octene	MeOH	7.4
diphenylacetylene	MeOH	7.6
butenediol	MeOH	7.6
1-heptene	MeOH	7.7
1,3-cyclohexadiene	MeOH	7.7
butynediol	H_2O	7.9
trans-stilbene	MeOH	8.5
fumaronitrile	MeOH	8.7
3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid)	MeOH	9.0
allyl alcohol	H_2O	9.4

[a] 5% water was used to dissolve $K_4[Pt_2(pop)_4]$. [b] From least squares analysis of Stern-Volmer plots; units of k_q are M^{-1} s^{-1}.

As with ketone triplets we do not expect that any particular alkene or alkyne will cause quenching of $Pt_2(pop)_4^{4-*}$ by a unique pathway. Instead we anticipate that quenching will occur by a combination of pathways having different rates.

The quenching rate data for a series of alkenes and alkynes with the triplet state of $Pt_2(pop)_4^{4-*}$ are shown in Table I.[7] These second-order rate constants (k_q) cover the range from 10^4 to 10^8 M^{-1} s^{-1}. The smallest rate constants are found with nonconjugated alkenes that have simple alkyl substituents. These alkenes all have high triplet energies (E_t > 70 kcal mol^{-1}), and therefore cannot be involved in energy transfer from the $^3A_{2u}$ state of $Pt_2(pop)_4^{4-*}$

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(7) Emission intensity data were collected on a SPEX fluorolog fluorimeter with a DATAMATE computer. Solutions were contained in Spectrocell Corp. fluorimeter tubes having screw top seals. The incident wavelength was 368 nm, and the observing wavelength was 514 nm. Intensities of the emission band against quencher concentration were measured for constant $[Pt_2(pop)_4^{4-}]$. These data were fitted to the Stern-Volmer equation $I_0/I = 1 + k_q\tau^\circ[Q]$ (where $[Q]$ is the quencher concentration, τ° is the lifetime of pure $Pt_2(pop)_4^{4-}$ in aqueous solution (1.25 μs) or in methanol (0.32 μs), and k_q is the rate constant to be measured). The complex used is $K_4Pt_2(pop)_4 \cdot 2H_2O$ which was dissolved in either water (purified by distillation from glass), or in the minimum volume of water (5%) with the organic solvent (usually methanol) added to the aqueous solution of the complex. The alkenes or alkynes used were high-purity reagents. Purification, where necessary, was by distillation or recrystallization. Because of the rather slow quenching rates it was necessary to use high (~0.2 M) concentrations of quencher reagent. This condition leads to somewhat greater errors in the rate data because the emission intensities are more likely to be affected by medium effects from the presence of the quencher. The solutions were not rigorously deoxygenated since we found that the presence of oxygen did not introduce significant errors in the quenching rate constants.

(8) Electron density moves from the $\sigma^*(d_z2)$ orbital of $Pt_2(pop)_4^{4-}$ to the $\sigma(p_z)$ orbital of $Pt_2(pop)_4^{4-*}$; see: Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571-4575. Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489-3494. Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061-7064.

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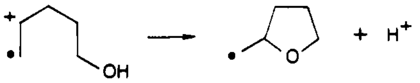
Table II. Rate Constants for the Reaction of the Benzophenone Triplet with Alkenes

alkenes or alkyne	log $k_q{}^a$	ref
1-octene	6.6	13
norbornene	7.6	21
cyclooctene	7.9	13
cyclohexene	7.9	13
1,5-cyclooctadiene	7.9	13
fumaronitrile	7.9	18
ethyl vinyl ether	7.9	22
trimethylethylene	8.6	21
tetramethylethylene	9.0	21
tetraethoxyethylene	9.6	23

[a] Measured in benzene solvent except for ethyl vinyl ether, which was measured in Freon; units of k_q are M^{-1}/s^{-1}.

(E_t = 57.7 kcal mol^{-1}).[6] The excited state of $\mathrm{Pt_2(pop)_4^{4-*}}$ has increased Pt–Pt bonding over that found in the ground state, thereby making this $^3A_{2u}$ state more electrophilic for binding of alkene and alkyne donor ligands into the axial coordination positions.[8] Quenching by electron transfer from alkene to $\mathrm{Pt_2(pop)_4^{4-*}}$ does *not* appear to be a viable mechanism for explaining the observed quenching rates, since increasing the alkyl substitution at the alkene bond, and thereby the electron density of the alkene, does not cause increased quenching rates (cf. 1-, 2-, and 3-hexene). Furthermore we find that the photolysis of a mixture of $\mathrm{Pt_2(pop)_4^{4-}}$ and 4-pentenol for 12–18 h does *not* lead to the formation of 2-methyltetrahydrofuran, the ring closure product expected to be rapidly formed from the intermediate carbonium ion produced in a photoredox mechanism (eq 1). Charge-transfer quenching by electron transfer from $\mathrm{Pt_2(pop)_4^{4-*}}$ to the alkene or alkyne is not a major pathway, as evidenced by the low quenching rate for maleic acid.



(1)

For the simplest alkyl-substituted alkenes that have strong C–H bonds, we propose that the quenching pathway involves diradical formation. Such a mechanism corresponds to that observed for the triplet state of benzophenone. For the case of $\mathrm{Pt_2(pop)_4^{4-*}}$ the product from $\mathrm{R_2C{=}CR_2}$ will be $\dot{\mathrm{P}}\mathrm{t_2(pop)_4C_2}\dot{\mathrm{R}}\mathrm{_4^{4-}}$. This intermediate cannot undergo the ring closure observed with benzophenone, but will revert back to $\mathrm{Pt_2(pop)_4^{4-}}$ and $\mathrm{R_2C{=}CR_2}$ (eq 2) with loss of energy. This diradical quenching pathway will be

$$\mathrm{Pt_2(pop)_4^{4-*} + R_2C{=}CR_2 \rightarrow \dot{P}t_2(pop)_4CR_2\dot{C}R_2^{4-} \rightarrow Pt_2(pop)_4^{4-} + R_2C{=}CR_2} \quad (2)$$

the most favored for alkenes such as styrene where the coordinated organic radical is stabilized by conjugation.

For the alkenes and alkynes which react with $\mathrm{Pt_2(pop)_4^{4-}}$ by the faster rates, it appears that two pathways are operative. The first of these is hydrogen atom abstraction.[9] This mechanism is particularly favored for allyl alcohol, butenediol and butynediol, where the substituent group stabilization of the product radical results in lower C–H bond enthalpies.

$$\mathrm{Pt_2(pop)_4^{4-*} + CH_2{=}CHCH_2OH \rightarrow Pt_2(pop)_4H^{4-} + CH_2{=}CH\dot{C}HOH} \quad (3)$$

The triplet quenching rates for these complexes are among the highest observed for alkenes and alkynes with k_q being in the region of 10^7 M^{-1} s^{-1}. As support for these pathways we have investigated the reaction between the $^3A_{2u}$ state of $\mathrm{Pt_2(pop)_4^{4-*}}$ and allyl alcohol. The transient difference spectrum of this aqueous solution shows the presence of two products, $\mathrm{Pt_2(pop)_4H^{4-}}$ with λ_{max} = 340 nm formed by hydrogen atom abstraction, and a second product with λ_{max} = 310 nm, which we tentatively assign to $\dot{\mathrm{P}}\mathrm{t_2(pop)_4}\dot{\mathrm{R}}^{4-}$ (R = $\mathrm{CH_2{-}\dot{C}HCH_2OH}$).

The second mechanism is energy transfer.[8] This pathway is possible for alkenes and alkynes that have triplet energies which are equal to or smaller than that of the $^3A_{2u}$ state of $\mathrm{Pt_2(pop)_4^{4-*}}$. The triplet energy of this diplatinum(II) complex is 57.7 kcal mol^{-1}.[6] Two alkenes which have triplet energies below this are *trans*-stilbene (E_t = 50 kcal mol^{-1}) and 1,3-cyclohexadiene (E_t = 52.4 kcal mol^{-1}),[10] and these alkenes with the respective quenching values of 2.2×10^7 and 4.0×10^6 M^{-1} s^{-1} for k_q are two of the more reactive alkenes. By contrast *cis*-stilbene with a triplet energy of 57 kcal mol^{-1} reacts at a slower rate ($k_q = 1.2 \times 10^6$ M^{-1} s^{-1}),[9,11] even though for an inner-sphere energy-transfer mechanism the cis isomer will preferentially complex to platinum over the trans isomer.

Using transient difference spectroscopy we have obtained direct evidence for the formation of the triplet excited states of *trans*-stilbene, tetraphenylethylene, and diphenylacetylene by energy-transfer photosensitization from the $^3A_{2u}$ state of $\mathrm{Pt_2(pop)_4^{4-}}$ (eq 4).[10] These excited states are identified by the observation of transient absorption bands at 375, 380, and 390 nm, respectively.[12]

$$\mathrm{Pt_2(pop)_4^{4-*} + \mathit{trans}\text{-}PhCH{=}CHPh \rightarrow Pt_2(pop)_4^{4-} + PhCH{=}CHPh^*} \quad (4)$$

By comparison with the $^3A_{2u}$ state of $\mathrm{Pt_2(pop)_4^{4-*}}$, the triplet state of benzophenone (E_t = 69.2 kcal mol^{-1})[11] shows a similar chemistry with alkenes and alkynes. For alkenes with allylic hydrogens the triplet state of benzophenone, like the $^3A_{2u}$ state of $\mathrm{Pt_2(pop)_4^{4-*}}$, will abstract hydrogen atoms.[13] Energy-transfer quenching occurs with coumarin,[14] dienes,[15] and piperylene,[16] and the benzophenone triplet reacts with 2-butene or other simple alkenes by diradical formation.[17] Quantitatively the *rates* of reaction of the benzophenone triplet with alkenes are either faster or slower than we find with $\mathrm{Pt_2(pop)_4^{4-*}}$ (Table II),[11,18] but the respective alkyne rates are comparable.[19,20] These rate differences show that there is a higher selectivity for the reaction of alkenes with $\mathrm{Pt_2(pop)_4^{4-*}}$ than with $\mathrm{Ph_2CO^*}$. This selectively where 1-octene and fumaronitrile react faster with $\mathrm{Pt_2(pop)_4^{4-*}}$ correlates with an inner-sphere pathway, since these alkenes are the ones that are expected to bind most strongly to platinum.

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Registry No. Tetramethylethylene, 563-79-1; maleic acid, 110-16-7; *trans*-3-hexene, 13269-52-8; cyclooctene, 931-88-4; 1,1-diphenylethylene, 530-48-3; 1,5-cyclooctadiene, 111-78-4; cyclohexene, 110-83-8; ethyl vinyl ether, 109-92-2; 2-hexene, 592-43-8; 4-pentenol, 821-09-0; styrene, 100-42-5; 2,5-dimethyl-3-hexyne-2,5-diol, 142-30-3; 1,5-hexadiene, 592-42-7; *cis*-stilbene, 645-49-8; acetylenedicarboxylic acid, 142-45-0; 1-hexyne, 693-02-7; 1-hexene, 592-41-6; 1-octene, 111-66-0; diphenylacetylene, 501-65-5; butenediol, 110-64-5; 1-heptene, 592-76-7; 1,3-cyclohexadiene, 592-57-4; butynediol, 110-65-6; *trans*-stilbene, 103-30-0;

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fumaronitrile, 764-42-1; squaric acid, 2892-51-5; allyl alcohol, 107-18-6; $K_4[Pt_2(pop)_4]$, 79716-40-8.

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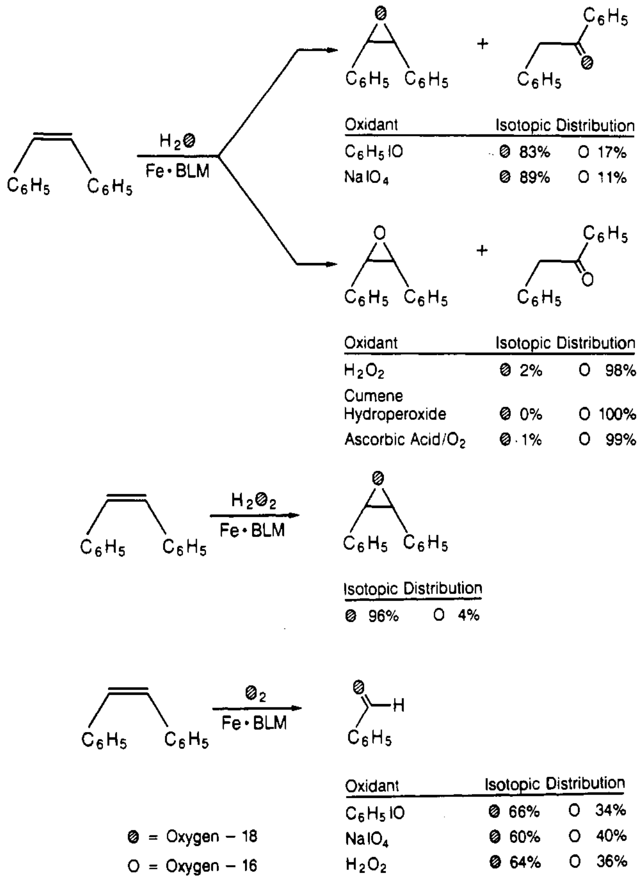
Mechanism of Oxygenation of *cis*-Stilbene by Iron Bleomycin

Sir:

The bleomycins (BLM's) are a family of antitumor antibiotics isolated from *Streptomyces verticillus*.[1] They mediate DNA strand scission in the presence of O_2 and certain metal ions;[2] this transformation is believed to constitute the basis for their antitumor activity.[3] Metallobleomycins may also be activated for DNA strand scission by the use of oxidants such as iodosobenzene.[4] In addition to mediating destruction of DNA, activated metallobleomycins have been shown to effect the oxidation of several low molecular weight olefinic substrates.[4a,4c,5]

Although the products[1a,6] and chemical mechanism[1a,6,7] of DNA cleavage by bleomycin have been studied in some detail, as have the products resulting from BLM-mediated oxidation of small molecules,[4a,4c,5] the only published oxygen-labeling experiments identified the aqueous medium as the source of oxygen in *cis*-stilbene oxide formed in the C_6H_5IO-supported oxidation of *cis*-stilbene by FeBLM.[5b] Presently, we report the results of a more thorough study in which we employed oxygen labeling to help define the mechanism of small-molecule oxidation by BLM. The results of this study suggest that the source of oxygen transferred in the formation of *cis*-stilbene oxide is a metal–oxo species, the oxygen in which is derived from the oxidant employed for metallobleomycin activation.

Scheme I. Isotopic Distribution of ^{18}O and ^{16}O in Products Resulting from FeBLM-Dependent Oxidation of *cis*-Stilbene in the Presence of Various Oxidants[10]



Oxidant	Isotopic Distribution	
C_6H_5IO	⊘ 83%	O 17%
$NaIO_4$	⊘ 89%	O 11%

Oxidant	Isotopic Distribution	
H_2O_2	⊘ 2%	O 98%
Cumene Hydroperoxide	⊘ 0%	O 100%
Ascorbic Acid/O_2	⊘ 1%	O 99%

Isotopic Distribution	
⊘ 96%	O 4%

Oxidant	Isotopic Distribution	
C_6H_5IO	⊘ 66%	O 34%
$NaIO_4$	⊘ 60%	O 40%
H_2O_2	⊘ 64%	O 36%

When carried out under aerobic conditions, the FeBLM-mediated oxidation of *cis*-stilbene afforded a number of products, including *cis*-stilbene oxide and benzaldehyde.[4,5,8] Previous work suggested that these two products resulted from two different oxidation pathways: one of these was suggested to be an oxygen-transfer reaction leading to *cis*-stilbene oxide; the other, an electron-abstraction pathway yielding the stilbene cation radical, which reacted with O_2 to form benzaldehyde.[8] The oxygen-18-labeling data presented in Scheme I are consistent with this hypothesis.[9] For each of the oxidants tested, the benzaldehyde oxygen was derived primarily from O_2.[10] In contrast, the source of oxygen in *cis*-stilbene oxide depended on the oxidant used to support the reaction. In all cases, the labeling of deoxybenzoin

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[9] In a typical $H_2{}^{18}O$-labeling experiment, 22 μL of an aqueous solution containing preformed 9.1 mM Fe^{III}BLM was added to an (aerobic) solution that had been formed by admixture of 150 μL of methanol containing 100 mM *cis*-stilbene and 285 μL of 4:1 CH_3OH–$H_2{}^{18}O$ (50% ^{18}O content in H_2O). The reaction was initiated by the addition of 50 μL of 4:1 CH_3OH–$H_2{}^{16}O$ containing 40 mM oxidant. The reaction mixture was maintained at 25 °C for 1 h and then treated with 2 mL of 0.5% aqueous NaCl. The reaction mixture was extracted with 1 mL of CH_2Cl_2, and the organic extract was concentrated and analyzed on a 15 m DB-17 column in a Finnigan-MAT 4610 gas chromatograph–mass spectrometer equipped with an INCOS data system. Reactions conducted under $^{18}O_2$ (^{18}O content 98%) were performed similarly, with the exception that the reaction mixtures were degassed by alternate cycles of vacuum/argon purging in capped 1-mL reacti-vials (Wheaton Scientific) prior to addition of the oxidant. Following addition of $^{18}O_2$ via gastight syringe to a final pressure of approximately 1 atm, a degassed solution of oxidant was added to initiate the reaction.

[10] In addition to the exchange of the C_6H_5CHO oxygen with H_2O under the reaction conditions (23%), some C_6H_5CHO formation was also observed to occur in a BLM- and Fe-independent fashion. Therefore, the ^{18}O-labeling efficiency of C_6H_5CHO by the oxidative pathway envisioned[8] is significantly understated in Scheme I.

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