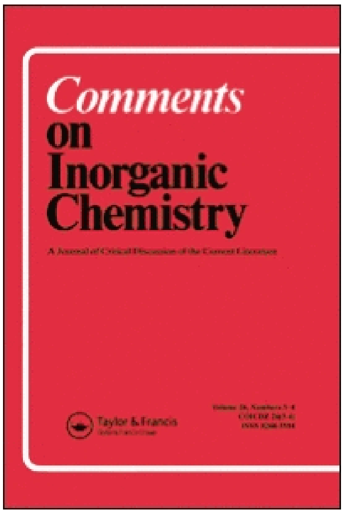

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Excited State Properties of $Rh_2(O_2CCH_3)_4$: Solution Photochemistry and Photoinitiated DNA Cleavage

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The photophysical properties of $Rh_2(O_2CCH_3)_4(L)_2$ ($L = CH_3OH$, THF = tetra-hydrofuran, PPh_3 = triphenylphosphine, py = pyridine) were explored upon excitation with visible light. All the complexes exhibit a long-lived transient absorption signal ($\tau = 3.5 - 5.0$ μs) assigned as an electronic excited state of each molecule. An optical transition at ~760 nm is observed in the spectra of the transients, whose position is relatively independent of axial ligand. No emission from the $Rh_2(O_2CCH_3)_4(L)_2$ ($L = CH_3OH$, THF, PPh_3, py) systems was observed at room temperature or at 77 K, but energy transfer from excited $Rh_2(O_2CCH_3)_4(PPh_3)_2$ to tetracene and perylene takes place to form the $^3\pi\pi^*$ excited state of each acceptor. Electron transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ to dimethyl viologen (MV^{2+}) and chloro-p-benzoquinone (Cl-BQ) takes place with quenching rate constants (k_q) of 8.0×10^6 $M^{-1}s^{-1}$ and 1.2×10^6 $M^{-1}s^{-1}$ in methanol, respectively. A k_q value of 2×10^8 $M^{-1}s^{-1}$was measured for the quenching of the excited state of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ by O_2 in methanol. The results of the energy and electron transfer experiments are consistent with the production of an excited state of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ with energy, E_{00}, between 1.34 eV and 1.77 eV. The excited state of $Rh_2(O_2CCH_3)_4$ is not able to undergo hydrogen abstraction chemistry. However, the photoproduced one-electron oxidized complex, $Rh_2(O_2CCH_3)_4^+$, is able to convert isopropanol to acetone and to efficiently cleave DNA with $\lambda_{irr} \leq 610$ nm.

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INTRODUCTION

Photoexcitation of bridged bimetallic d^7-d^7 and d^8-d^8 complexes with visible light is known to result in the formation of reactive diradical species, schematically shown in Figure 1.[1–5] The homolytic bond cleavage resulting in metal-centered radicals is found often in the photochemistry of bridged and non-bridged d^7-d^7 bimetallic systems, including $(Rh^{II})_2$, $(Re)_2$, $(Mn)_2$, and $(Pt^{III})_2$ complexes. Although the d^8-d^8 $(Pt^{II})_2$ and $(Rh^{I})_2$ systems do not possess a formal metal-metal bond in the ground state, light excitation often results in the formation of a partial metal-metal bond in the excited state which exhibits diradical properties when the two metal centers are held in close proximity by the bridging ligands. The radical nature of the excited states of these d^7-$d^7$and d^8-d^8 systems has been shown to result in atom abstraction from various substrates. A background discussion of the reported photophysical properties and photochemical transformations observed for various bimetallic complexes is presented below.

Our work focuses on the excited state properties and photoreactivity of dirhodium(II) tetraacetates, $Rh_2(O_2CCH_3)_4(L)_2$, with various axial ligands, L (CH_3OH, H_2O, PPh_3 = triphenylphosphine, py = pyridine, THF = tetrahydrofuran), and related complexes, as well as the exploration of the potential role of these molecules as anti-tumor agents and in photodynamic therapy. $Rh_2(O_2CR)_4(L)_2$ complexes have long been known,[6] and the structure, bonding, and reactivity of the complexes have been extensively investigated.[7,8] Dirhodium tetracarboxylates are known to catalyze many reactions including cyclopropanation,[9] alkyne cyclopropenation,[10] C-H insertion,[11] and carbeonid initiated C-C bond formation.[12] However, these are examples of ground state reactions that are not initiated by light. The d^7-d^7 $Rh_2(O_2CCH_3)_4(L)_2$ complexes were chosen for our initial studies because they are known to bind DNA and are insensitive to water and O_2.

Excited State Properties of d^7-d^7 Bimetallic Complexes

It has long been known that irradiation of bimetallic d^7-d^7 complexes results in metal-metal bond homolysis, thus producing metal-centered mononuclear radicals.[1–5] Prominent examples include $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$,[13] which undergo metal-metal bond cleavage upon irradiation into their $\sigma \rightarrow \sigma^*$ transition in the near-uv.[14,15] Early evidence for

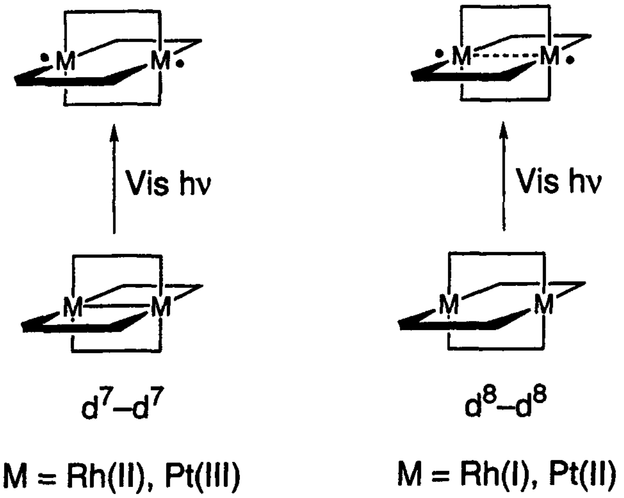


FIGURE 1 Schematic representation of the diradical formation in the excited states of d^7-d^7 (left) and d^8-d^8(right) bimetallic complexes

this reactivity included the formation of the $MnRe(CO)_{10}$ cross product upon photolysis of mixtures $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ as well as the ability to trap the photogenerated $\bullet M(CO)_5$ fragments with various radical traps.[16,17] More recently, $\bullet Mn(CO)_5$ and $Mn_2(CO)_9$ were observed utilizing time-resolved techniques, resulting from the photoinduced Mn-Mn bond homolysis and CO loss, respectively.[18] Similar intermetallic bond photocleavage is observed for $Fe_2(Cp)_2(CO)_2(\mu\text{-}CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$),[19] where CO-loss photochemistry also competes with metal-metal bond cleavage.[20,21] In addition, $Rh_2(CH_3CN)_{10}{}^{4+}$ is a recent example of this type of photoreactivity, since irradiation with $\lambda_{irr} > 435$ nm results in the initial formation of $\bullet Rh(CH_3CN)_5{}^{2+}$ radicals, which were shown to recombine to regenerate the starting material following several steps.[22]

In d^7-d^7 bimetallic systems where bridging ligands are utilized to hold the two metals in close proximity, excited states have been observed and characterized. Several bridged bimetallic $(Rh^{II})_2$ complexes are emissive and undergo metal-centered diradical reactions upon excitation of their dσ* excited states.[23] For example, solid samples of $Rh_2(dfpma)_3Cl_4$ (dfpma = bis(difluorophosphino)methylamine) and

$Rh_2\{MeN[P(OEt^{F3})_2]_2\}_3Cl_4$ ($MeN[P(OEt^{F3})_2]_2$ = bis(bis(trifluoroethoxy)phosphine)methylamine) are emissive a room temperature with phosphorescence maxima at 821 nm (τ = 250 μs) and 819 nm (τ = 350 μs), respectively.[24] This behavior is similar to that observed for bridged d^7-d^7dirhenium complexes, including $Re_2(CO)_6(dmpm)_2$ [dmpm = bis(dimethylphosphino) methane)] complex.[25]

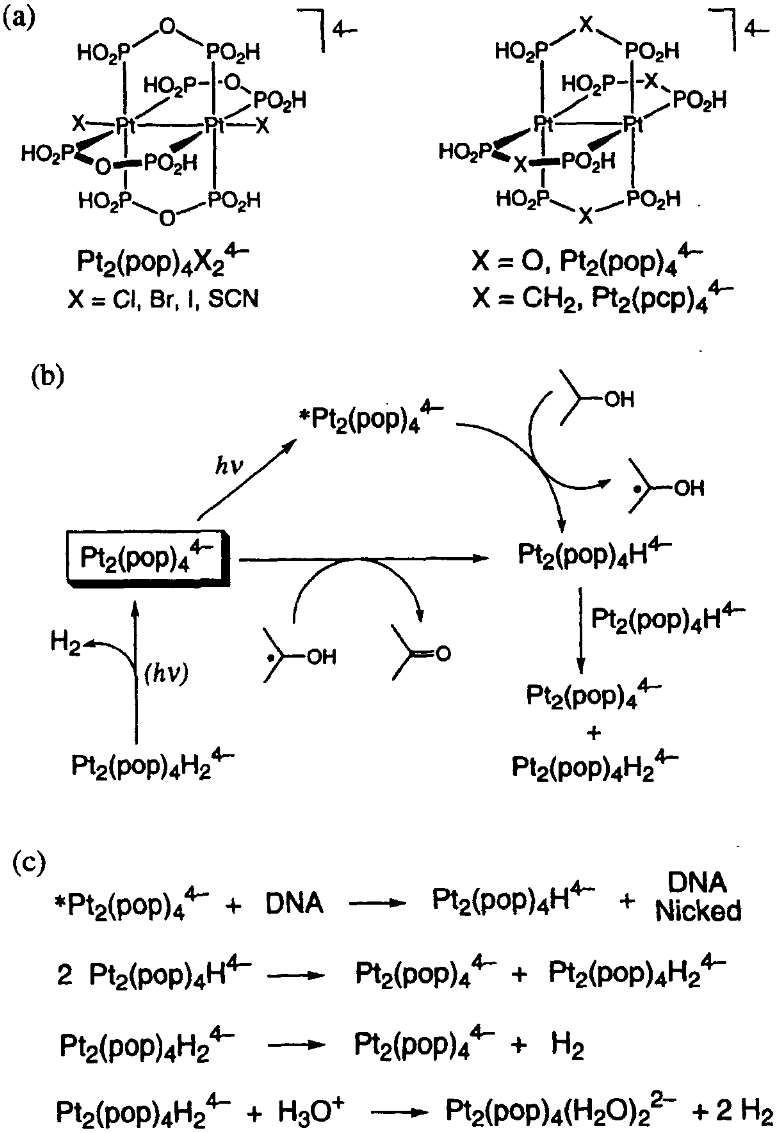
There are also a few examples in the literature of emission and photoreactivity by bridged diplatinum(III) complexes. The pyrophosphite-bridged $Pt_2(pop)_4X_2^{4-}$ (pop = $HO_2POPO_2H^{2-}$; X = Cl, Br, SCN) systems and $Pt_2(pop)_4(py)_2^{2-}$ (structures shown in Figure 2a) exhibit emission maxima ranging from 685 nm to 754 nm with lifetimes of 15–20 μs at 77 K.[26] No emission from the complexes was observed at room temperature, but a long vibrational progression in the emission of $Pt_2(pop)_4Br_2^{4-}$ at 5 K with vibrational spacing of 125 cm^{-1} was observed. This evidence together with vibrational data led to the conclusion that the excited state possessed dσ* character, with a large distortion along the Pt-Pt bond.[26] In addition, the long lifetime of the excited state is consistent with intersystem crossing from a triplet excited state to the singlet ground state. Halide substitution reactions were shown to be accelerated by light in the $Pt_2(pop)_4X_2^{4-}$ (X = Cl, Br, I) complexes, where the observations were best explained by Pt^{III}-Pt^{III} bond homolysis upon dσ* excitation.[27] It was later discovered that solid tetraphosphate-bridged $Pt_2(HPO_4)_4L_2^{n-}$ (L = Cl, Br, n = 4; L = H_2O, n = 2) complexes were emissive at room temperature with maxima at 702 nm, 678 nm, and 694 nm for L/n = Cl/4, Br/4, and H_2O/2, respectively, and lifetimes ranging from 330 ns to 700 ns at 298 K and 1.2 μs to 37 μs at 77 K.[28] In addition, diplatinum(III) complexes bridged by sulfates, such as $Pt_2(SO_4)_4(H_2O)_2^{2-}$ and $Pt_2(SO_4)_4Cl_2^{4-}$exhibit weak emission at 694 nm (τ = 450 ns) and 755 nm (τ = 290 ns), respectively, at 77 K.[29] In both types of complexes the luminescence is believed to involve a dσ* excited state. The preparation, electronic absorption, electronic structure calculations on $Pt_2(O_2CCH_3)_4^{2+}$ were reported more recently,[30] however, the complex does not appear to be emissive.

Photophysical Properties of d^8-d^8 Bimetallic Complexes

The excited states of various d^8-d^8 bimetallic systems have also been explored, where the most prominent examples are complexes of Rh(I), Ir(I), and Pt(II).[31,32] Binuclear Rh(I) and Ir(I) isocyanide complexes, with ground state $(d\sigma^*)^2$ configuration, possess singlet and triplet $(d\sigma^*)^1(p\sigma)^1$ excited states.[30,33] Room temperature acetonitrile solutions of $Rh_2(b)_4^{2+}$ (b = 1,3-diisocyanopropane) and $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) exhibit fluorescence at 656 nm and 614 nm, respectively, and phosphorescence at 865 nm and ~780 nm, respectively.[34] The singlet and triplet excited states of Rh(I) and Ir(I) bimetallic complexes were also observed utilizing transient absorption techniques.[35] Furthermore, spectroscopic evidence for the shortening of the Rh(I)-Rh(I) bond in the excited state of $Rh_2(TMB)_4^{2+}$ and $Rh_2(dimen)_4^{2+}$ (dimen = 1,8-diisocyanomenthane) has been reported,[36] consistent with the partial metal-metal bond formation in the excited state of d^8-d^8 bimetallic complexes as shown in Figure 1.

The luminescent d^8-d^8 diplatinum(II) complex $Pt_2(pop)_4^{4-}$ (structure shown in Figure 2a) has been extensively investigated, and its lowest excited state with $(d\sigma^*)^1(p\sigma)^1$electron configuration has been shown to be reactive towards various substrates.[32,37] Excitation of $Pt_2(pop)_4^{4-}$ at 367 nm in water results in fluorescence at 407 nm (τ = 40 ps) and phosphorescence at 517 nm (τ = 9.8 μs) measured at room temperature, corresponding to the ${}^1A_{2u}\rightarrow{}^1A_{1g}$ and ${}^3A_{2u}\rightarrow{}^1A_{1g}$ transitions, respectively.[38,39] Excited state emission was also observed for other diplatinum(II) complexes, such as $Pt_2(CN)_4(\mu\text{-dppm})_2$ (dppm = bis(diphenyl-phosphinomethane) and $Pt_2(pcp)_4^{4-}$ (pcp = $HO_2PCH_2PO_2H^{2-}$).[40,41] The triplet excited state lifetime of $Pt_2(pcp)_4^{4-}$ (τ = 55 ns at 298 K) is much shorter than that of $Pt_2(pop)_4^{4-}$, however, the emission of both complexes is quenched by various alkyl and aryl halides, hydrogen atom donors, oxidants, reductants, alkenes, and alkynes.[41]

The long-lived triplet excited state of $Pt_2(pop)_4^{4-}$ has been shown to abstract hydrogen atoms from C-H, P-H, Si-H, and Sn-H bonds, where the axial $Pt_2(pop)_4H^{4-}$ intermediate was detected.[42] Benzyl alcohol and diphenylmethanol undergo hydrogen-atom transfer quenching of the $Pt_2(pop)_4^{4-}$ triplet emission with quenching rate constants of 2.0×10^7 $M^{-1}s^{-1}$ and 2.5×10^6 $M^{-1}s^{-1}$, respectively.[41] The hydrogen atom abstraction by ${}^*Pt_2(pop)_4^{4-}$ from isopropanol takes place with $k_q = 1.0\times10^5$ $M^{-1}s^{-1}$, which is the initial step in the catalytic conversion of isopropanol to acetone and H_2.[41,43] The mechanism for this photocatalytic conversion is shown in Figure 2b. The catalytic α-hydrogen abstraction reactivity by ${}^*Pt_2(pop)_4^{4-}$ will later be compared to that observed by us for $Rh_2(O_2CCH_3)_4$. Similar conversion of 1-phenyletha-



$$^{*}Pt_2(pop)_4^{4-} + DNA \longrightarrow Pt_2(pop)_4H^{4-} + \begin{matrix}DNA\\ Nicked\end{matrix}$$

$$2\ Pt_2(pop)_4H^{4-} \longrightarrow Pt_2(pop)_4^{4-} + Pt_2(pop)_4H_2^{4-}$$

$$Pt_2(pop)_4H_2^{4-} \longrightarrow Pt_2(pop)_4^{4-} + H_2$$

$$Pt_2(pop)_4H_2^{4-} + H_3O^{+} \longrightarrow Pt_2(pop)_4(H_2O)_2^{2-} + 2\ H_2$$

FIGURE 2 (a) Molecular structures of $Pt_2(pop)_4X_2^{4-}$ and $Pt_2(pop)_4^{4-}$. Mechanism for the (a) photocatalytic conversion of isopropanol to acetone (see references 41–43) and (b) DNA photocleavage (see references 44–46) by $^{*}Pt_2(pop)_4^{4-}$

nol to acetophenone involving hydrogen abstraction by the triplet excited state of $Pt_2(pop)_4^{4-}$ was also reported.[44] In addition to the efficient quenching of the $Pt_2(pop)_4^{4-}$ triplet excited state by alkyl and aryl halides, $^*Pt_2(pop)_4^{4-}$ was recently reported to undergo excited state halogen atom transfer from halogenated anionic complexes of the type $Co(CN)_5X^{3-}$ (X = Cl, Br, I, N_3) via a reductive mechanism, resulting in the formation of $Pt_2(pop)_4X_2^{4-}$.[45]

Furthermore, hydrogen abstraction from the DNA backbone upon photoexcitation of $Pt_2(pop)_4^{4-}$ was reported, which results in DNA photocleavage.[44] The reaction with calf-thymus DNA proceeds via hydrogen atom abstraction, with the formation of $Pt_2(pop)_4H^{4-}$ and $Pt_2(pop)_4H_2^{4-}$, where the latter reacts with H_3O^+ to form the observed diplatinum(III) $Pt_2(pop)_4(H_2O)_2^{2-}$ complex and H_2 (schematically shown in Figure 2c).[46] The cleavage of duplex DNA by the triplet excited state of $Pt_2(pop)_4^{4-}$ is not enhanced by piperidine treatment, consistent with hydrogen abstraction rather than with a mechanism involving guanine oxidation.[47] In model systems, it was shown that the complex reacts with nucleic acids and nucleotides through 4′- and 5′-hydrogen abstraction from the deoxyribose backbone.[44] However, the overall negative charge of the complex precludes it from binding to the double helix slowing the bimolecular rate of photocleavage ($k \sim 10^5$-$10^6 M^{-1}s^{-1}$), thus making the process inefficient.

THERMAL AND LIGHT ACTIVATION OF ANTITUMOR AGENTS

Photodynamic Therapy Mediated by $^1O_2$

Photodynamic therapy (PDT) has received a great deal of attention recently owing to the ability of the technique to target tumor tissue selectively.[48–55] After a nontoxic and inactive drug is applied topically or injected intravenously it localizes in tumor tissue, and it can be photoactivated with visible light. This procedure results in the selective death of cancerous cells without affecting normal tissue. Some of the molecules utilized in PDT studies, pre-clinical trials, and current treatments include derivatives of metallated (Zn, Al) and free-base porphyrins, chlorins, benzoporphyrins, and phthalocyanins.[48,51] In addition, Photofrin® is a mixture that contains hematoporphyrin and hematoporphyrin derivative that has been recently approved by the U.S. Food and Drug Administration for the treatment of advanced esophageal and early lung cancer.[51] However, a critical limitation of Photofrin® is its retention by the skin for several weeks following treatment causing persistent cutaneous photosensitivity.[48,52]

Oxygen plays a key role in photodynamic therapy. Photoactivation of the drugs in the presence of oxygen results in reactive species, largely believed to be $^1O_2$ (singlet oxygen), although superoxide and hydroxyl radicals may also play a role in the photochemistry. The initial excitation of the photosensitizer drug produces its short-lived singlet state ($\tau \sim$ 1–12 ns), which quickly deactivates to the long-lived triplet excited state ($^3\pi\pi^*$) with typical lifetimes in the microsecond to millisecond timescale.[53–55] Energy transfer from this $^3\pi\pi^*$ state to ground-state $^3O_2$ results in the formation of the lowest excited state of oxygen, $^1O_2$.[53–55] As long as oxygen is available within the cell, $^1O_2$ generated by the photoactivated drugs can cause oxidative damage to biomolecules including proteins, nucleic acids, and membrane lipids.[42] One particular drawback of the systems derived from porphyrins and phthalocyanins is that in the absence of oxygen the excited states themselves are not reactive. Therefore, when the oxygen in the vicinity of the photosensitizer is consumed, the drug becomes inactive until O_2 can diffuse once again into the cell or reactive area.[48]

Enediyne Drugs

Calicheamicin, esperamicin, and dynamicin are examples of potent antitumor antibiotics currently used for the treatment of various cancers.[56–58] The structures of some individual members of each of these families of drugs are shown in Figure 3a. The success of these complex molecules is attributed to the presence of the enediyne functionality, found in common in these drugs. The mode of action of the enediyne moiety is centered on its ability to undergo the Bergman cycloaromatization (Figure 3b).[59–62] As shown in Figure 3b, a diradical species is formed as an intermediate in the cyclization. This intermediate is crucial in the ability of the molecules to simultaneously abstract hydrogen atoms from each deoxyribose strand when the drugs are bound to DNA.[56–66] The activation of these enediyne antibiotics can be thermal or chemical. In Dynemicin A (Figure 3b), for example, bioreduction triggers the Berg-

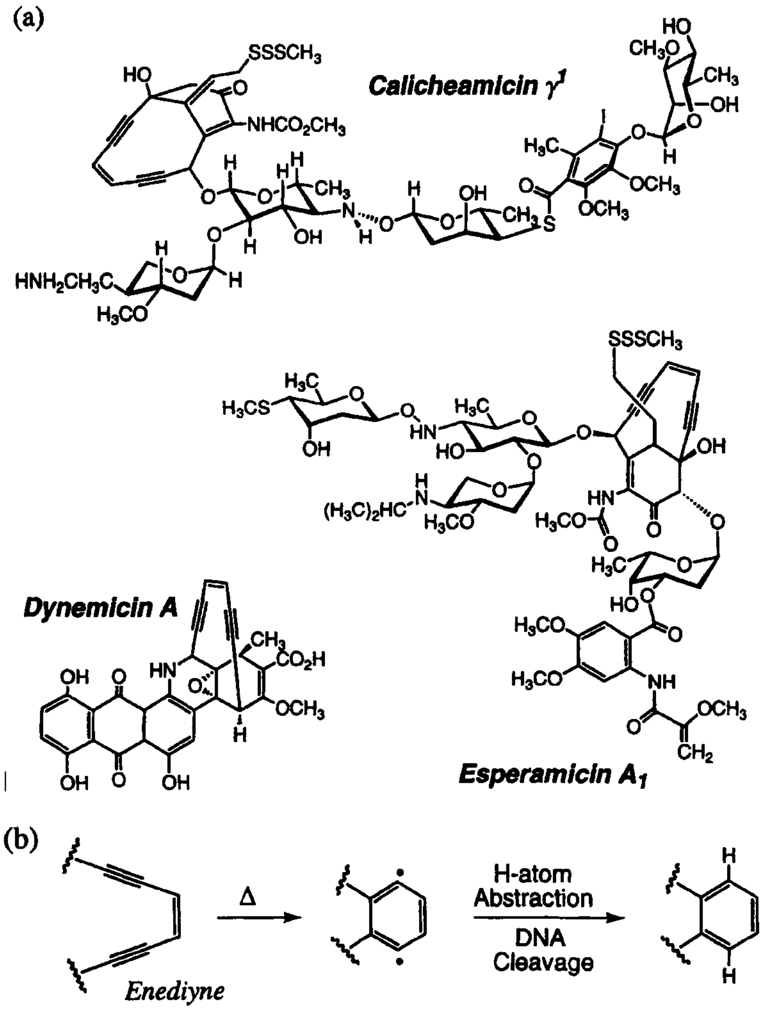


FIGURE 3 (a) Molecular structures of various enediyne antitumor drugs and (b) Bergman cyclization of the enediyne functionality through a diradical intermediate

man cycloaromatization. The Bergman cycloaromatization in drug-duplex adducts results in a double-strand cut that ultimately leads to cell death.[56–67] Similar DNA cleavage is also known for the related antibiotic neocarzinostatin, where chemical activation also results in the formation of a diradical intermediate.[68,69] In addition, many thermally or chemically activated synthetic diradical-forming enediyne mimics have been explored, however, it is difficult to control the activation in these drugs.[70–72] The use of low energy photons presents an alternative means to activate the drugs, which can be easily controlled.

Photoactivated Enediyne Analogs

Photoinitiation of the Bergman cycloaromatization can provide a means to "turn on" the DNA cleavage and antitumor activity through sole irradiation of affected areas and tumors. Photoinduced diradical formation can be attained upon direct excitation of enediynes, but requires the utilization of damaging ultraviolet (uv) and near-uv light.[73–75] The photochemical reaction is further complicated by the competing thermal cyclization and the possible activation *in vivo* by bioreductive agents.[73] There have been several reports by various researchers on other photoinitiated diradical-forming organic reagents that could be utilized as photodynamic therapy agents.[76–81] Unfortunately these organic photoreagents also require uv or near-uv excitation ($\lambda_{exc} \leq 450$ nm).[76–81] It is well known that for useful tissue penetration of the radiation $\lambda_{irr} > 600$ nm is required, where irradiation at 630 nm and 690 nm result in tissue penetration of approximately 0.5 cm and 1 cm, respectively.[48] Therefore, in the exploration of new molecules it is desirable that the excited state leading to the reactive intermediates, such as diradicals, be accessed with $\lambda_{exc} > 600$ nm.

Our interest in the excited state reactions of the d^7-d^7 and d^8-d^8 bimetallic systems arises from their reactive diradical excited states and their ability to absorb low-energy photons. These complexes could potentially be used in photodynamic therapy for the treatment of cancerous cells without the need for the production of $^1O_2$, where photoactivation of the complex selectively delivered to the carcinoma can result in damage that can ultimately lead to cell death. The diradical excited states of the d^7-d^7 and d^8-d^8 bimetallic complexes could, in principle, parallel the mode of action of the enediyne family of antitumor agents. Thus these complexes could represent a photoactivated form of enediyne analogs. For the bimetallic complexes to be useful in these studies, they must not be sensitive to water or oxygen. This requirement precludes the use of the diphosphine-bridged systems discussed above.

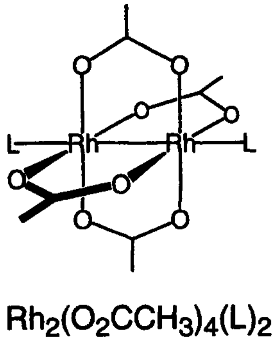


FIGURE 4 Molecular structures of $Rh_2(O_2CCH_3)_4(L)_2$ complexes

DIRHODIUM TETRAACETATES

DNA Binding and Model Systems

The d^7-d^7 $Rh_2(O_2CCH_3)_4$ complex (structure shown in Figure 4) is known to bind duplex DNA and to inhibit DNA replication.[82] In addition, the related $Rh_2(O_2CR)_2(N\text{-}N)_2^{2+}$ (R = PhCH(OH), $CH_3CH(OH)$; N-N = 1,10-phenanthroline, 2,2′-bipyridine) systems have recently been shown to act as antibacterial agents and to exhibit cytostatic activity against human oral carcinoma.[83] Various model systems of the binding of nucleic acids to the $Rh(O_2CCH_3)_4$ core have been recently synthesized and crystallographically characterized, where complexes possessing both axial and bridging nucleobases were isolated.[84,85] Substituted adenines and adenosines typically bind $Rh_2(O_2CCH_3)_4$ as axial ligands, whereas guanines have been shown to coordinate as bridging ligands across the rhodium-rhodium bond when reacted with $Rh_2(O_2CCH_3)_2(CH_3CN)_6^{2+}$.[86,87] In addition, $Rh_2(O_2CCH_3)_2$ $(CH3CN)_6^{2+}$ was recently shown to bind as dirhodium bis-acetate units to GG and AA sites on single-stranded oligonucleotides.[88] The direct reaction of $Rh(O_2CCH_3)_4(L)_2$ and related tetracarboxylate dirhodium complexes themselves with adenine and adenosine result in the formation of the axially-coordinated complex. To obtain bridging coordination of nucleic acids, replacement of two of the bridging carboxylates in

$Rh(O_2CCH_3)_4$, such as in $Rh_2(O_2CCH_3)_2(CH_3CN)_6{}^{2+}$, is necessary prior to the reaction with the nucleobases, nucleotides, or nucleosides.

Although model complexes derived from the $Rh(O_2CCH_3)_4$ core have been prepared and characterized with nucleic acids in the ligation sphere, as well as adducts with single-stranded oligonucleotides, the mode of binding of the $Rh(O_2CCH_3)_4$ complexes to the double helical DNA remains unclear.

Electronic Structure

Long-lived excited states have not been previously reported by others for the dirhodium(II) tetracarboxylates, although there have been numerous experimental and theoretical reports on the electronic structure of these complexes.

Prior studies have demonstrated that variation of the axial ligands, L, can lead to dramatic shifts in the peaks of the electronic absorption spectra of the $Rh_2(O_2CR)_4(L)_2$ complexes.[89–92] The absorption spectra of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ and $Rh_2(O_2CCH_3)_4(PPh_3)_2$ are shown in Figure 5.[93] The spectra were interpreted with the aid of electronic structure calculations on the complexes, which indicate significant mixing between the axial Rh-L σ interactions and the Rh-Rh σ and σ^* molecular orbitals (MOs), as well as mixing between the low-lying carboxylate π and π^* systems and the metal-centered MOs of the Rh_2(II,II) bimetallic core.[94,95] Ground-state IR and resonance Raman spectroscopic studies have also been utilized to gain insight into the electronic structure of the $Rh_2(O_2CR)_4(L)_2$ complexes.[96] Assignment of the lowest energy transition as RhRh π^* to RhRh σ^* has been made for all the $Rh_2(O_2CCH_3)_4(L)_2$ complexes, independent of the axial ligand, L. Emission from these complexes has not been reported by others or detected by us.

The calculated molecular orbital energy ordering of the metal-centered orbitals in $Rh_2(O_2CCH_3)_4$ with no axial ligands is shown in the center of Figure 6.[94,95,97] The symmetric and antisymmetric linear combinations of the axial ligand lone pair orbitals, ϕ_1 and ϕ_2, are of the appropriate symmetry to interact with the RhRh σ and RhRh σ^* MOs of the $Rh_2(O_2CCH_3)_4$ core, where the changes in the orbital energies as a function of axial coordination by H_2O and PPh_3 are depicted in Figure 6. As shown in Figure 6, calculations predict that axial coordina-

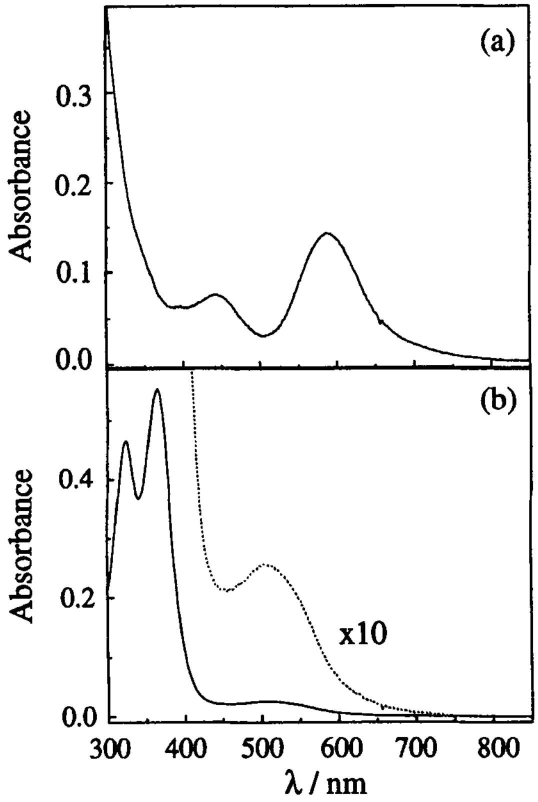


FIGURE 5 Ground state electronic absorption spectra of (a) $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ and (b) $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in CH_3OH

tion would not affect the energy of the δ^* HOMO (highest occupied molecular orbital) significantly,[94,95] but that in $Rh_2(O_2CCH_3)_4(PPh_3)_2$ (where PH_3 was used in the calculations) the HOMO would have mostly Rh-P (phosphorous lone pair) character (ϕ_1 in Figure 6).[94] The difference in energy of the H_2O and PPh_3 lone pairs results in a greater interaction of ϕ_2 with RhRh σ in the former and of ϕ_1 with RhRh σ^* in the latter (see Figure 6).[94,95]

Following these theoretical predictions, EPR experiments on the one-electron oxidized $[Rh_2(O_2CCH_3)_4(PPh_3)_2]^+$ showed that indeed the

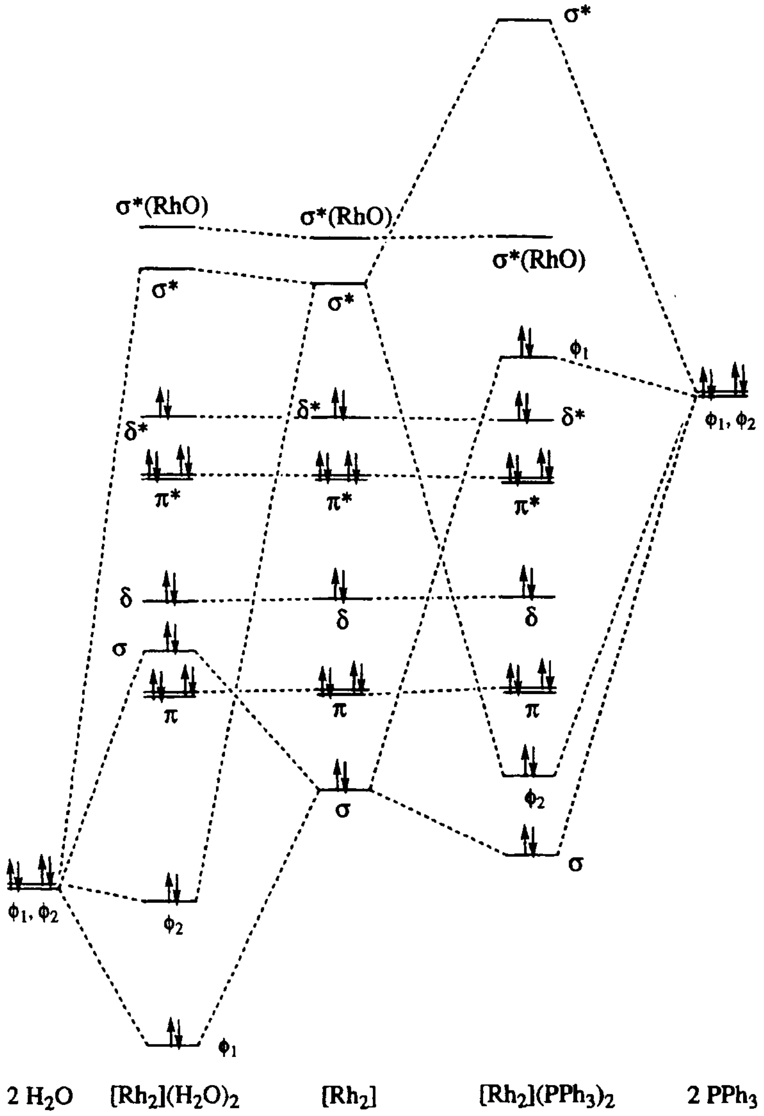


FIGURE 6 Changes in the MO diagram of $Rh_2(O_2CR)_4$ = [Rh_2] (center), upon axial ligation by water (left) and PPh_3(right)

SOMO (singly occupied molecular orbital) in the cation is Rh-P σ.[98] In contrast, EPR spectra of $[Rh_2(O_2CCH_3)_4(H_2O)_2]^+$ were consistent with the odd electron residing in a π* orbital.[99] This finding was inconsistent with the earlier electronic structure calculation shown in Figure 6 for the L = H_2O complex, however, the calculations predict that the δ* and π* orbitals are close in energy.[94–96] From the EPR spectra, crystal structure data, electrochemical measurements, and recent electronic structure calculations on a large number of $Rh_2(B)_4(L)_2^+$ (B = bridging ligand, L = axial ligand) systems and their neutral precursors a picture of the factors that govern the orbital ordering in these systems has emerged. A summary of the electron configuration of the bridged $Rh_2(B)_4(L)_2^+$ complexes is shown in Figure 7.[100]

$[Rh_2(B)_4(L)_2]^+$ Complex	Electron Configuration
(1) Strong σ-donating axial ligand, L	
B = carboxylates **L = phosphines, phosphites**	$\pi^4\,\delta^2\,\pi^{*4}\,\delta^{*2}\sigma^1$
(2) π-Donating bridging ligands, B	
B = anions of amides, amidines, o-hydroxy- or o-aminopyridines	$\sigma^2\,\pi^4\,\delta^2\,\pi^{*4}\,\delta^{*1}$
(3) Weakly π-Donating bridging ligands, B, and weakly σ-donating axial ligand, L	
B = carbolylates, sulfate **L = water, THF, alchols, acetone, nitriles, chloride**	$\sigma^2\,\pi^4\,\delta^2\,\delta^{*2}\,\pi^{*3}$

FIGURE 7 Electron configurations of various known $[Rh_2(B)_2(L)_2]^+$ complexes

Excited State Properties and Energy Transfer

The $Rh_2(O_2CCH_3)_4$ complexes were prepared by reported methods,[5,91,96b] and the instrumentation used has been previously described.[101] No emission was observed from methanol solutions of $Rh_2(O_2CCH_3)_4(L)_2$ (L = CH_3OH, PPh_3, py) in the 500 nm to 1,100 nm spectral region at room temperature, and at 77 K in methanol or as a solid between 500 and 850 nm. To our knowledge, there have been no previous reports of emission from $Rh_2(O_2CCH_3)_4$.

Although the $Rh_2(O_2CCH_3)_4$ complexes do not emit light, upon excitation with a short laser pulse a transient absorption signal is observed on the microsecond timescale. Figure 8 presents the transient absorption spectrum of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in CH_3OH collected ~500 ns following the 532 nm (FWHM ~10 ns, 5 mJ/pulse) excitation laser pulse, similar to that obtained with 355 nm excitation. The return of the transient signal at ~760 nm to the baseline ($\Delta OD = 0$) could be fit to a monoexponential decay with lifetime of 5.0 μs. Similar spectral profiles with a peak at ~760 nm were collected for $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in CH_3OH ($\tau = 4.4$ μs) and in CH_2Cl_2 ($\tau = 4.6$ μs). The transient absorption spectra of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = THF, py) complexes in methanol exhibit similar spectral profiles to that shown in Figure 8 with monoexponential lifetimes of 3.5 μs and 4.8 μs, respectively, measured at 760 nm. The decay of the transient spectrum of each species in a given solvent is independent of probe wavelength in the 300 nm to 850 nm range. Based on the decay of the absorption at 760 nm, the lifetime of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in methanol is independent of the concentration of rhodium complex (60 μM to 600 μM) and excitation pulse energy (6 mJ/pulse to 16 mJ/pulse).

The results described above provide some evidence as to the identity of the observed transient. Many transient species observed upon excitation of metal complexes are known to be due to the loss of a ligand.[1,3] Photochemical loss of an axial ligand in the complexes can be ruled out, since the use of CH_3OH or CH_2Cl_2 as solvents has essentially no effect on the decay kinetics of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$. Additionally, the spectra and decay characteristics of $Rh_2(O_2CCH_3)_4(L)_2$ (L = THF, py, PPh_3) complexes are very similar to that of the complex with L = CH_3OH in methanol, although THF, py, and PPh_3 are significantly less labile than CH_3OH.[102] The possibility that the transient arises from the loss of one or more acetate ligands or from the conversion of a bridging acetate to a η^1-chelating ligand at a single Rh(II) center has also been ruled out because the addition of a large excess (0.6 M) of NaO_2CCH_3 to a methanol solution of 100 μM $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ does not change the decay kinetics of the transient.

The transient absorption spectrum of each of the complexes in the series $Rh_2(O_2CCH_3)_4(L)_2$ (L = CH_3OH, THF, py, PPh_3) exhibits a peak with a maximum in the 750 nm to 760 nm spectral region, and strong

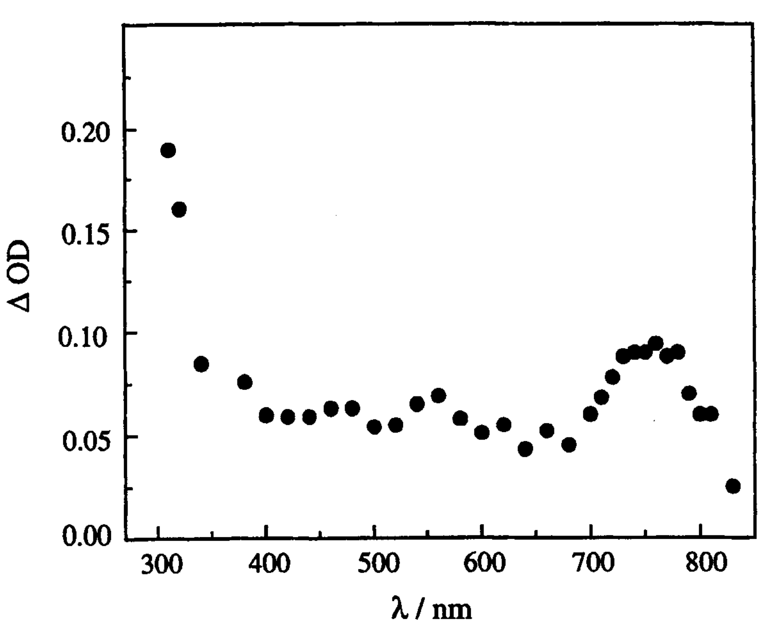


FIGURE 8 Transient absorption spectrum of 300 μM $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in CH_3OH collected 500 ns after excitation (λ_{exc} = 532 nm, ~10 mJ/pulse)

absorption at $\lambda < 400$ nm, as shown in Figure 8 for the complex with L = PPh_3. It is interesting to note that the absorption spectra of the oxidized $Rh_2(O_2CCH_3)_4(L)_2^+$ dinuclear complexes possess a peak at 755 nm (ε = 249 $M^{-1}cm^{-1}$) for L = H_2O and 775 nm (ε =187 M^{-1} cm^{-1}) for L = CH_3OH.[95b,100] However, in $Rh_2(O_2CCH_3)_4(PPh_3)_2^+$ this peak shifts to 538 nm,[95a] inconsistent with the transient signal arising from the cation formed upon photoexcitation. In addition, the decay kinetics of the transient at 760 nm are monoexponential, the lifetime of the transient is independent of initial concentration of Rh_2(II,II) complex, of laser light intensity, and of solvent (CH_2Cl_2 and CH_3OH), all of which would be expected to affect the recombination kinetics of the oxidized Rh_2(II,III) complex with the solvated electron or other species in solution.

Unequivocal evidence for the formation of an excited state of the $Rh_2(O_2CCH_3)_4(L)_2$ complexes upon excitation is imparted by the observed energy transfer from ${}^{*}Rh_2(O_2CCH_3)_4(PPh_3)_2$ to the ${}^{3}\pi\pi^{*}$ of organic acceptors possessing various excited state energies. Upon excitation of ${}^{*}Rh_2(O_2CCH_3)_4(PPh_3)_2$ in the presence of tetracene ($E_{00}({}^{3}\pi\pi^{*}) = 1.24$ eV)[103] with 532 nm, the spectrum of the ${}^{3}\pi\pi^{*}$ excited state of tetracene is observed with its characteristic millisecond lifetime (Figure 9a). Excitation of tetracene alone with 532 nm does not result in the production of its triplet excited state, however, it can easily be generated with 355 nm excitation (Figure 9b). Energy transfer was also observed from ${}^{*}Rh_2(O_2CCH_3)_4(PPh_3)_2$ to perylene ($E_{00}({}^{3}\pi\pi^{*}) = 1.30$ eV)[103,104] and to O_2 ($E_{00}({}^{1}\Delta_g) = 1.0$ eV)[105] in methanol, but not to diphenylanthracene ($E_{00}({}^{3}\pi\pi^{*}) = 1.77$ eV)[103,106] or phenothiazine ($E_{00}({}^{3}\pi\pi^{*}) = 2.62$ eV).[103,107]

Since the photoinduced formation of ground state transient intermediates can be ruled out, we believe that the observed transient arises from an excited state of the complex. Although a precise assignment of the electronic transitions observed in the spectrum of the excited state cannot be made at this time, some important points are discussed below. As described earlier, the energies of the Rh-Rh σ and σ^{*} orbitals are profoundly affected by the σ-donor ability of the axial ligands, which result in $(\pi^{*})^{3}$ and $(\sigma_{PPh3})^{1}$ electron configurations for the oxidized $Rh_2(O_2CCH_3)_4(L)_2^{+}$ complexes with H_2O and PPh_3 axial ligands, L, respectively. Notably, the transient spectra and lifetimes of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = CH_3OH, py, PPh_3, THF) systems are relatively invariant to the choice of axial ligand. This observation allows us to rule out the participation of the Rh-Rh σ and σ^{*} orbitals in the transitions of the excited state transient species. The lowest energy absorption of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = H_2O, CH_3OH, PPh_3) complexes has been assigned to the allowed π^{*} (e_g) $\rightarrow$ σ^{*} (a_{2u}) transition, thus initially creating a hole in the π^{*} orbital upon excitation. The transitions in the excited state of the complex may arise from metal-centered orbitals with π or δ parentage or acetate MOs to π^{*}, both of which are expected to be relatively independent of the axial ligands. The detailed assignment of the observed excited states is currently under investigation.

Photoinduced Electron Transfer

As shown in Figure 10, electron transfer to 4,4′-dimethyl viologen (MV^{2+}) is observed upon 532 nm excitation of $Rh_2(O_2CCH_3)_4(PPh_3)_2$

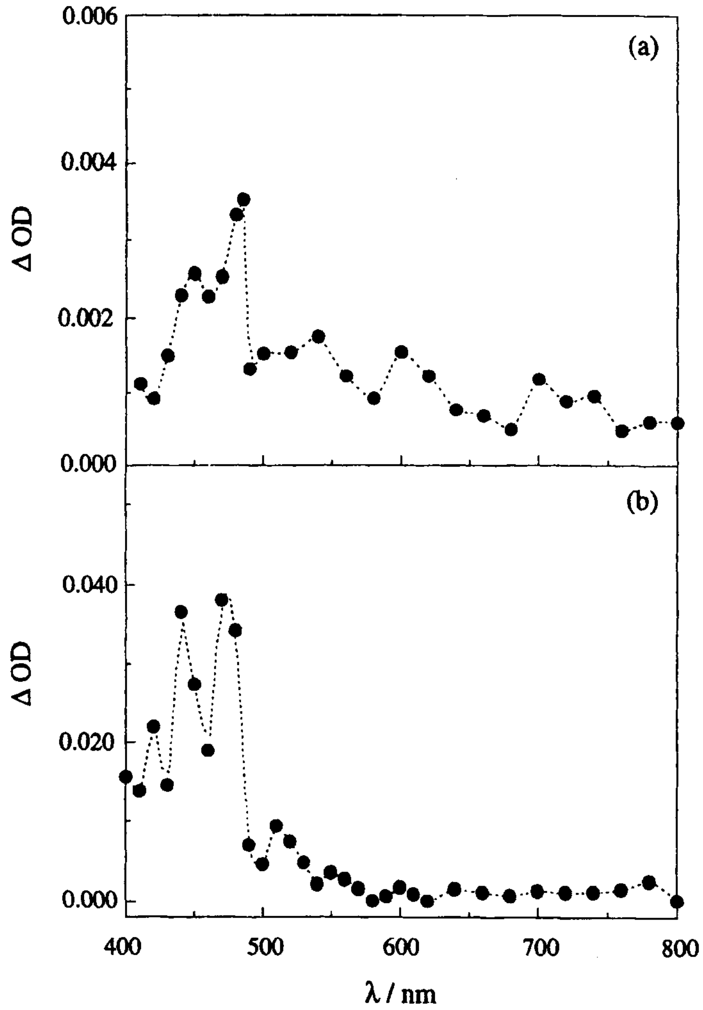


FIGURE 9 Transient absorption spectra of (a) 800 μM $Rh_2(O_2CCH_3)_4(PPh_3)_2$ with 200 μM tetracene in CH_3OH collected 11 μs after excitation (λ_{exc} = 532 nm, 10 mJ/pulse) and (b) 200 μM tetracene in CH_3OH collected 40 μs after excitation (λ_{exc} = 355 nm, 5 mJ/pulse)

in methanol, where the absorption peaks of $MV^{+\bullet}$ at 395 nm and 605 nm are observed in transient spectrum.[108] In addition, the broad spectral feature at ~540 nm can be assigned to the one electron oxidized complex, $Rh_2(O_2CCH_3)_4(PPh_3)_2{}^+$.[95a] Stern-Volmer plots of τ_o/τ vs [MV^{2+}], where τ_o and τ are the lifetimes of the $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ transient monitored at 760 nm in the absence and presence of quencher, respectively, result in a quenching rate constant, k_q of $8.0 \times 10^6\ M^{-1}s^{-1}$. Similarly, the oxidative quenching of the $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ transient by chloro-*p*-benzoquinone (Cl-BQ; $E_{1/2}(A^{0/-}) = -0.10$ vs NHE)[109] in methanol proceeds with $k_q = 1.2 \times 10^6\ M^{-1}s^{-1}$. Oxidative quenching of $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ was also observed in the presence of Ag^+ ($k_q = 5.0 \times 10^7\ M^{-1}s^{-1}$). In contrast, no electron transfer quenching of the $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ transient by 9,10-diphenylanthracene ($E_{1/2}(D^{+/0}) = +1.46$ V vs NHE)[106] or phenothiazine ($E_{1/2}(D^{+/0}) = +0.45$ V vs NHE)[110] was observed following 532 nm excitation.

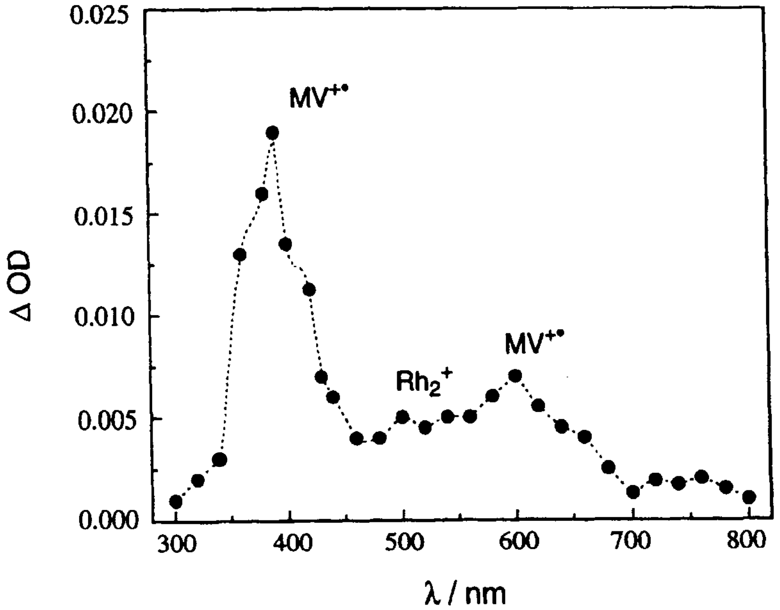


FIGURE 10 Transient absorption spectrum of 300 μM $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in CH_3OH in the presence of 5 mM $MV^{2+} \cdot 2BF_4^-$ (λ_{exc} = 532 nm, 10 mJ/pulse), collected 3.5 μs after excitation

Using the oxidation potential of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ (+0.88 V vs NHE)[111] and the reduction potential of MV^{2+} (-0.46 V vs NHE),[108] a value of $E_{00} \geq 1.34$ eV can be estimated for the dirhodium complex. The energy and electron transfer experiments place the excited state energy of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ between 1.34 eV and 1.77 eV.

Solution Photochemistry

No overall photochemistry was observed for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in methanol either in the presence or absence of electron acceptors. The electron transfer reactions described above are reversible, where the back electron transfer regenerates the ground state $Rh_2(O_2CCH_3)_4(PPh_3)_2$ complex. In contrast, when methanol solutions of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ were utilized in the quenching experiments with the electron acceptors described above, irreversible photochemistry took place. No chemical reactions were observed under same conditions in the dark or upon irradiation in methanol in the absence of electron acceptors. Photolysis of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ with visible light, $\lambda_{irr} > 515$ nm, in methanol in the presence of electron acceptors resulted in the formation of an insoluble black solid and in changes in the visible absorption spectrum of the solution. This photochemical reaction in the presence of electron acceptors was also observed when ethanol (EtOH) and isopropanol (i-PrOH) were used as solvents, but not in *t*-butylalcohol (t-BuOH) or DMF. This solvent dependence of the reactivity will be discussed later in this section.

The solid produced in these photochemical reactions of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ was isolated by filtration and XPS spectra were recorded. The XPS spectra of the solids collected from the reactions in MeOH and EtOH are consistent with the formation of a Rh(0) carbonyl cluster in the former and rhodium metal in the latter. The changes in the absorption spectrum of the solution are due to the formation of a Rh(III) monomeric species. Upon addition of excess phen (1,10-phenanthroline) to the filtered solutions, the $Rh(phen)_3^{3+}$ complex is formed. This photoreactivity observed in the presence of electron acceptors is similar to that reported for the chemical oxidation of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ by HCl(g) in methanol, where Rh(s) and Rh(III) were formed.[112] In contrast, when the oxidation of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ by HCl(g) is undertaken in ether, only the oxidized $RhCl_6^{3-}$ product is observed along with $H_2(g)$.[112] In addition, it was reported that the one-electron electrochemical oxidation of $Rh_2(O_2CCH_3)_4(H_2O)_2^+$ led to the formation of the original dimer and mononuclear Rh(III).[113] A possible mechanism for these results is the dissociation of the oxidized $Rh_2(II,III)^+$ complex into a stable Rh(III) complex and a •Rh(II) mononuclear radical. The •Rh(II) monomers can combine to regenerate the dinuclear $Rh_2(II,II)$ complex, however, in the presence of reducing agents, such as methanol, the •Rh(II) radical can be reduced to Rh(I), ultimately resulting in the formation of Rh(s). It should be pointed out that in pulse radiolysis experiments where Rh(II) mononuclear radicals were formed, it was found that slow ligand loss was accompanied by a rapid reduction of the metal to a stable Rh(I) complex in the presence of reducing agents.[114]

In order to further understand the mechanistic aspects of the observed photoreactivity, we prepared the Rh(II,II) complex $Rh_2(CH_3CN)_{10}^{4+}$ and the Rh(I) monomer $Rh(CH_3CN)_4^+$ by methods previously reported.[22] Photolysis of $Rh_2(CH_3CN)_{10}^{4+}$ with visible light in CH_3CN results in the initial formation of two $•Rh^{II}(CH_3CN)_5^{2+}$ radical fragments following the homolytic Rh-Rh bond cleavage.[22] It was shown that in acetonitrile the starting material is recovered after ~2 hrs.[22] In contrast, when the $Rh_2(CH_3CN)_{10}^{4+}$ complex is photolyzed ($\lambda_{irr} > 435$ nm) in methanol, the formation of Rh(0) is observed. This reaction does not take place in the dark. Similarly, irradiation of the Rh(I) complex $Rh(CH_3CN)_4^+$ with visible light in methanol results in the production of Rh(s), whereas no reactivity is observed in the dark. These findings show that the stable Rh(I) complexes lead to the formation Rh(s) when irradiated in the presence a reducing agent such as methanol. The Rh(II) mononuclear radicals initially produced upon photolysis of $Rh_2(CH_3CN)_{10}^{4+}$ are likely to form the Rh(I) species in the presence of methanol, which can be further photolyzed to produce Rh(s). If the pulse radiolysis data is utilized as a guide, it may be postulated that the conversion of Rh(II) radicals to Rh(I) complex is not light activated.

Although the mononuclear Rh(III) complexes and Rh(s) are the final products, clearly the alcohol used as solvent plays a role in the reactivity. As shown in Figure 11, the ^1H NMR spectra of benzene-d_6 solutions of 40 μM $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in the presence of 200 μM Ag^+as an electron acceptor and 8 mM i-PrOH results in the photocatalytic production of acetone ($\lambda_{irr} > 515$ nm). Although some acetone is already present in the t = 0 spectrum, we found that this was due to room light.

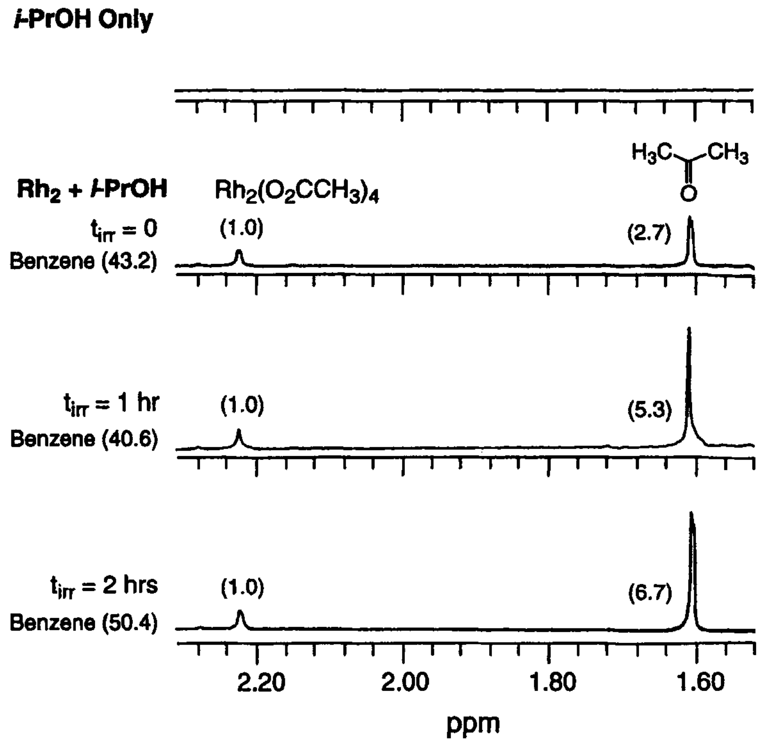


FIGURE 11 ^1H NMR spectra (400 MHz) collected at various times, t, during the photolysis ($\lambda_{irr} \geq 515$ nm) of 40 μM $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in the presence of 200 μM Ag^+ as electron acceptor and 8 mM i-PrOH in benzene-d6 as solvent (see text)

When the sample is kept completely in the dark, only a very small amount of acetone is observed (integrations of 1.0 and 0.2 for the $Rh(O_2CCH_3)_4$ and acetone protons, respectively), which does not change when left in the dark for 2 hrs. A comparison of the integration of the acetate protons in $Rh_2(O_2CCH_3)_4$ with those of acetone in Figure 11 reveals that ~14-fold molar excess of acetone is produced after irradiation for 2 hrs, therefore, the conversion is catalytic. In these experiments the benzene protons from the solvent are used as an internal integration standard to monitor decomposition of the rhodium complex.

These values are shown in Figure 11, where the $Rh_2(O_2CCH_3)_4$: benzene ratio does not change within experimental error.

The catalytic production of acetone from isopropanol by $Rh_2(O_2CCH_3)_4$ in the presence of electron acceptors under irradiation with visible light likely proceeds via the photoinduced formation of the one electron oxidized $Rh_2(O_2CCH_3)_4^+$ complex. We prepared $Rh_2(O_2CCH_3)_4^+$ independently through bulk electrolysis, followed by isolation and purification. The ^1H NMR spectra of a benzene-d_6 solution of 200 μM $Rh_2(O_2CCH_3)_4^+$ in the presence of 2 mM i-PrOH results in the quantitative formation of acetone relative to the starting Rh_2 complex.

It is proposed that the mechanism of conversion of i-PrOH to acetone by $Rh_2(O_2CCH_3)_4^+$ parallels that reported for $^*Pt_2(pop)_4^{4-}$ discussed earlier and shown in Figure 2b.[41,43] In this system, the radical excited state of the diplatinum complex is able to abstract α-hydrogen atoms from alcohols, including isopropanol, thus forming the axially coordinated hydride $Pt_2(pop)_4H^{4-}$ intermediate. In the reactivity of the $Rh_2(O_2CCH_3)_4^+$ complexes presented here, a labile axial ligand is necessary for the conversion of i-PrOH to acetone.

From our observations presented above and the evidence reported in the literature a tentative mechanism for the photoreactivity of the $Rh_2(O_2CCH_3)_4$ complexes can be proposed. $Rh_2(O_2CCH_3)_4^+$ is formed from the long-lived $^*Rh_2(O_2CCH_3)_4$ excited state in the presence of electron acceptors and it is able to quantitatively convert i-PrOH to acetone, regenerating the ground state $Rh_2(O_2CCH_3)_4$ starting material, which can then absorb another photon to continue the cycle. The observed Rh(III) mononuclear species and the Rh(s) may be due to the formation of Rh(III) and Rh(II) monomers as a decomposition product of $Rh_2(O_2CCH_3)_4^+$. As discussed above, the Rh(II) radical can react with methanol to form a Rh(I) complex, and the latter can be photoexcited in methanol to form Rh(s). In this scheme, the decomposition of $Rh_2(O_2CCH_3)_4^+$ into the monomer species represents the termination of the catalytic cycle. Further studies designed to elucidate the mechanism of the conversion of i-PrOH to acetone by $Rh_2(O_2CCH_3)_4^+$ are currently underway.

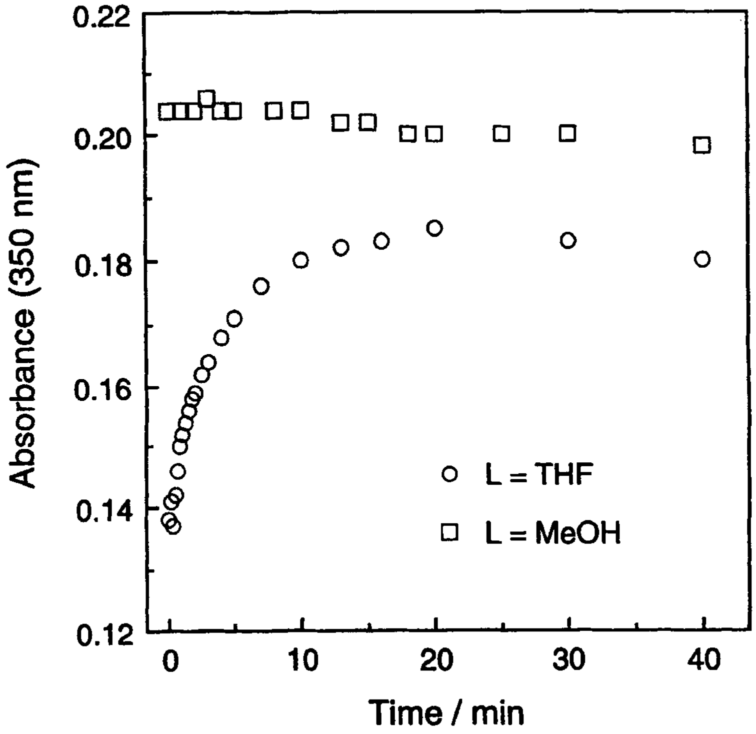


FIGURE 12 Changes in the absorption at 350 nm observed as a function of time upon the addition of $Rh_2(O_2CCH_3)_4(L)_2$ from a methanol stock solution to water with CH_3OH and THF axial ligands, L

DNA Photocleavage

Our interest in elucidating the hydrogen abstraction mechanism by $Rh_2(O_2CCH_3)_4^+$ in solution was driven by our observations of DNA photocleavage by $Rh_2(O_2CCH_3)_4(L)_2^+$ (L = CH_3OH, H_2O). It should be pointed out that no DNA photocleavage was observed for complexes with non-labile axial ligands, such as py and PPh_3. In addition, the photocleavage of duplex DNA by $Rh_2(O_2CCH_3)_4(THF)_2$ was only observed if the complex was left in either water or the solution containing plasmid and buffer for ~30 min prior to irradiation. The changes in

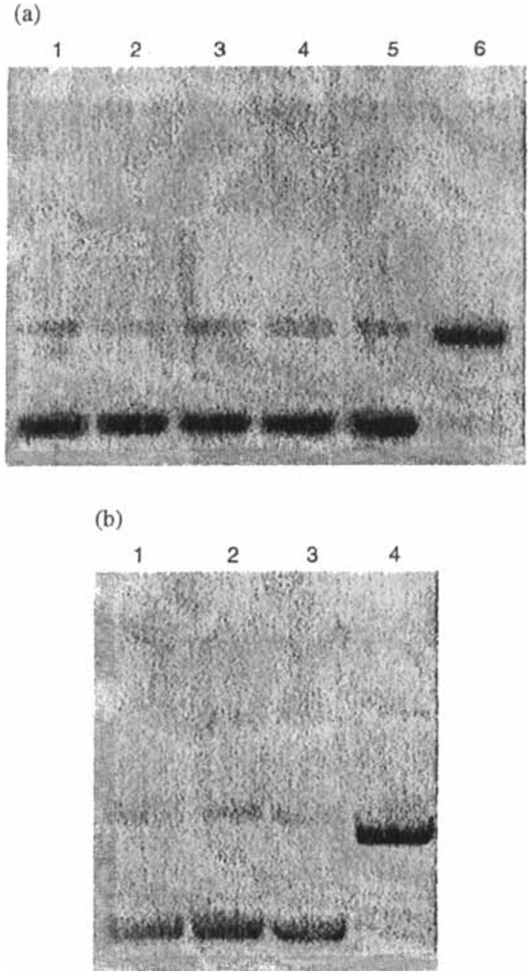


FIGURE 13 Imaged agarose gels showing the photocleavage of 100 μM pUC18 plasmid (5 mM Tris buffer, pH = 7.5) by Rh_2 ($Rh_2 = Rh_2(O_2CCH_3)_4(CH_3OH)_2$) in the presence of (a) 2 mM py^+, 40 μM Rh_2, 10 min irradiation, $\lambda_{irr} \geq 395$ nm and (b) 20 mM AQ^{2-}, 25 mM Rh_2, 15 min irradiation, $\lambda_{irr} \geq 450$ nm. (a) Lane 1: plasmid only, dark; Lane 2: plasmid only, irradiated; Lane 3: plasmid + Rh_2, irradiated; Lane 4: plasmid + py^+ irradiated; Lane 5: plasmid + Rh_2 + py^+, dark; Lane 6: plasmid + Rh_2 + py^+, irradiated. (b) Lane 1: plasmid only, dark; Lane 2: plasmid + Rh_2 + AQ^{2-}, dark; Lane 3: plasmid + AQ^{2-}, irradiated; Lane 4: plasmid + Rh_2 + AQ^{2-}, irradiated

the electronic absorption of the complex and ^1H NMR studies have shown that it takes ~20 min for complete exchange of the THF axial ligands with either H_2O or AMP (adenosine monophosphate). This exchange with water is shown in Figure 12, where the aqua-ligated complex $Rh_2(O_2CCH_3)_4(H_2O)_2$ absorbs more strongly at 350 nm than $Rh_2(O_2CCH_3)_4(THF)_2$. For comparison, the same study is plotted for $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in the same graph (Figure 12), where methanol is known to exchange rapidly with water (faster than the first measurement).[5,82] These results are important because they point at the necessity of a labile axial ligand for the DNA cleavage to take place. Since the complexes with non-labile axial ligands do not result in DNA cleavage, the following studies have been performed with $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ and will be referred to as Rh_2 throughout the discussion to follow.

Agarose gel electrophoresis shows that photoproduced $Rh_2(O_2CCH_3)_4^+$ is able to efficiently cleave double stranded DNA. The results of the trans-illuminated ethidium bromide stained agarose gel are shown in Figure 13 for the irradiation of Rh_2 and 100 μM (bases) of supercoiled plasmid pUC18 (5 mM Tris, pH = 7.5) with visible light in the presence of 20 mM anionic 1,8-antraquinone disulfonate (AQ^{2-}; λ_{irr} > 455 nm) and 2 mM cationic 3-cyano-1-metylpyridinium (py^+; λ_{irr} > 395 nm) electron acceptors. DNA cleavage is not observed if the solution is kept in the dark or upon irradiation of the Rh_2 complex alone with plasmid. Similar results were observed when 200 μM Ag^+ and 200 μM Fe^{3+} were utilized as the electron acceptors.

As discussed earlier, an important aspect of photodynamic therapy is for the potential drugs to absorb and react with $\lambda_{irr} \geq 600$ nm, where penetration of the radiation through the tissue is possible. Figure 14 shows the wavelength dependence of the DNA photocleavage by 2.5 μM Rh_2 and 100 μM plasmid in air (5 mM Tris, pH = 7.5) utilizing 2 mM py^+ as the electron acceptor. The irradiation wavelength was controlled by placing colored high-pass filters in front of the 150 W Xe arc lamp used in the photolysis. It is evident from Figure 14 that the cleavage remains efficient up through $\lambda_{irr} \geq 590$ nm, and a significant amount of cleavage is also observed for $\lambda_{irr} \geq 610$ nm. No photocleavage is evident at $\lambda_{irr} \geq 630$ nm.

The future design of $(Rh^{II})_2$ systems will focus on complexes that will be able to cleave DNA from their excited state directly through a radical mechanism. In addition, we will prepare complexes with DNA-binding

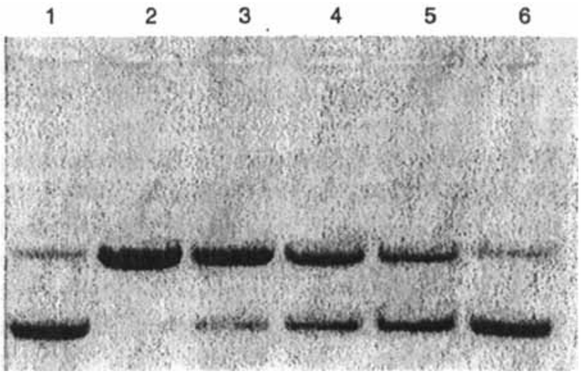


FIGURE 14 Imaged agarose gel showing the photocleavage of 100 μM pUC18 plasmid (5 mM Tris buffer, pH = 7.5) by 40 μM $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in the presence of 5 mM py^+ as a function of irradiation wavelength. Lane 1: plasmid only, dark; Lanes 2 – 6: plasmid + $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ photolyzed for 10 min with $\lambda_{irr} \geq 530$ nm (Lane 2), 570 nm (Lane 3), 590 nm (Lane 4), 610 nm (Lane 5), and 630 nm (Lane 6)

units in the ligation sphere and those that shift the absorption spectrum ~60 nm to lower energy, such that photocleavage with ~690 nm light is possible.

SUMMARY

The photophysical properties of $Rh_2(O_2CCH_3)_4(L)_2$ (L = CH_3OH, THF, PPh_3, py) were explored upon excitation with visible light. All the complexes possess a long-lived transient (3.5 to 5.0 μs) assigned as an electronic excited state of each molecule. The excited state exhibits an optical transition at ~760 nm independent of axial ligand. No emission from the $Rh_2(O_2CCH_3)_4(L)_2$ (L = CH_3OH, THF, PPh_3, py) systems was observed at room temperature or at 77 K, but energy transfer from excited $Rh_2(O_2CCH_3)_4(PPh_3)_2$ to tetracene and perylene takes place to form the $^3\pi\pi^*$ excited state of each acceptor. Electron transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ to MV^{2+} and Cl-BQ in methanol take place with quenching rate constants of 8.0×10^6 $M^{-1}s^{-1}$ and 1.2×10^6 $M^{-1}s^{-1}$, respectively. The quenching of the excited state of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ by O_2 proceeds with $k_q = 2\times10^8$ $M^{-1}s^{-1}$ in methanol. The observations are consistent with the production of an excited state of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ with energy, E_{00}, between 1.34 eV and 1.77 eV.

The excited state of $Rh_2(O_2CCH_3)_4$ is not able to undergo hydrogen abstraction chemistry. It is likely that, unlike $Pt_2(pop)_4^{4-}$, the excited state of the $Rh_2(O_2CCH_3)_4$ complexes is not diradical (or radical) in nature, possibly owing to the mixing of the acetate low-lying orbitals with metal-centered MO's. However, the photoproduced one-electron oxidized complex, $Rh_2(O_2CCH_3)_4^+$, is able to convert isopropanol to acetone and to efficiently cleave DNA with $\lambda_{irr} \leq 610$ nm.

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