# Excited-State Properties of $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py)

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The photophysical properties of $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF = tetrahydrofuran, $PPh_3$ = triphenylphosphine, py = pyridine) were explored upon excitation with visible light. Time-resolved absorption shows that all the complexes possess a long-lived transient (3.5−5.0 $\mu$s) assigned as an electronic excited state of the molecules, and they exhibit an optical transition at ~760 nm whose position is 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 detected, but energy transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ to the $^3\pi\pi^*$ excited state of perylene is observed. Electron transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ to 4,4′-dimethyl viologen ($MV^{2+}$) and chloro-*p*-benzoquinone (Cl-BQ) takes place with quenching rate constants ($k_q$) of $8.0 \times 10^6$ and $1.2 \times 10^6$ $M^{-1}$ $s^{-1}$ in methanol, respectively. A $k_q$ value of $2 \times 10^8$ $M^{-1}$ $s^{-1}$ 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 observations are consistent with the production of an excited state with excited-state energy, $E_{00}$, between 1.34 and 1.77 eV.

## Introduction

Dirhodium tetracarboxylates, $Rh_2(O_2CR)_4(L)_2$ (R = H, $CH_3$, $CH_2CH_3$), with various axial ligands, L, have long been known,[1] and the structure, bonding, and reactivity of the complexes have been extensively investigated.[2,3] The structures of the $Rh_2(O_2CCH_3)_4(L)_2$ complexes are shown in Figure 1. Dirhodium tetracarboxylates catalyze many reactions including cyclopropanation,[4] alkyne cyclopropenation,[5] C−H insertion,[6] and carbenoid-initiated C−C bond formation.[7] An important aspect of the $Rh_2(O_2CCH_3)_4$ complex is its ability to bind nucleic acids, single-stranded and duplex DNA,[8−10] to inhibit DNA replication,[8] and to photocleave DNA with visible light.[11] In addition, it was reported recently that the related $Rh_2(O_2CR)_2(N{-}N)_2^{2+}$ (R = PhCH(OH), $CH_3CH(OH)$; N−N = 1,10-phenanthroline, 2,2′-bipyridine) systems can act as antibacterial agents and exhibit cytostatic activity against human oral carcinoma.[12]

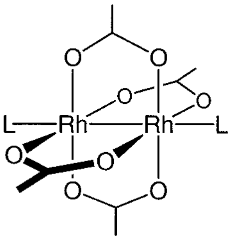

**Figure 1.** Molecular structure of $Rh_2(O_2CCH_3)_4(L)_2$ complexes.

Prior studies on $Rh_2(O_2CCH_3)_4(L)_2$ complexes have demonstrated that variation of the axial ligands, L, can lead to dramatic shifts in the peaks of the electronic absorption spectra of the complexes.[13−15] These results were interpreted with the aid of electronic structure calculations, which indicate significant mixing between the Rh−L $\sigma$ interactions and the Rh−Rh $\sigma$ and $\sigma^*$ molecular orbitals (MOs), as well as mixing between the low-lying carboxylate $\pi$ and $\pi^*$ systems and the metal-centered MOs of the $Rh_2$(II,II) bimetallic core.[16−18] Ground-state IR and resonance Raman spectroscopic studies have also been utilized

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to gain insight into the electronic structure of the $Rh_2(O_2CR)_4(L)_2$ complexes.[15b,19]

Although we have shown that $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ is able to photocleave duplex DNA upon irradiation with visible light ($\lambda_{irr} > 395$ nm) in the presence of electron acceptors,[11] to our knowledge, there have been no reports of a long-lived excited state of the $Rh_2(O_2CCH_3)_4$ complexes. The present work focuses on the properties of the excited states of $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF = tetrahydrofuran, $PPh_3$ = triphenylphosphine, py = pyridine), which can be accessed with visible light.

## Experimental Methods

**Materials.** $RhCl_3$, sodium acetate, $AgBF_4$, and $PPh_3$ were purchased from Aldrich and used without further purification. The $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) complexes were prepared by a modification of reported methods.[2,15b] $RhCl_3$ (0.4 mmol) and sodium acetate (2.4 mmol) were refluxed in ethanol/glacial acetic acid (10:1 v:v) for 2 h in the presence of slight excess $AgBF_4$ to remove chloride ions. The reaction mixture was dried immediately to prevent oxidation of the dirhodium complex by $Ag^+$, the solid was dissolved in boiling methanol, and solid AgCl was removed by filtration after cooling. Pure $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ was eluted from a silica gel column with methanol, thus separating the product from unreacted materials that remained in the column. Alternatively, $Rh_2(O_2CCH_3)_4$ was purchased from Aldrich and stirred in methanol with excess $AgBF_4$. The $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ was purified through a silica gel column following filtration. $Rh_2(O_2CCH_3)_4(L)_2$ complexes, with L = THF or py, were prepared by dissolving $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in THF or pyridine, respectively, following removal of the solvent. $Rh_2(O_2CCH_3)_4(PPh_3)_2$ was prepared by dissolving $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in methanol with slight excess of $PPh_3$, which results in precipitation of the product. Both methods of preparation of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ with the subsequent axial ligand substitution gave rise to identical photophysical properties for each complex. The $^1$H NMR, IR, and FAB mass spectra of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) are consistent with those previously reported for each complex.[2,15b]

**Instrumentation.** Absorption measurements were performed using a Hewlett-Packard diode array spectrometer (HP 8453) with HP8453 Win System software installed on a Gateway 2000 (E-4200) desktop computer. Emission spectra were collected on a SPEX FluoroMax-2 spectrometer equipped with a 150 W xenon source, a red-sensitive R928P photomultiplier tube, and DataMax-Std software on a Dell Optiplex GX1 microprocessor.

The transient absorption signal was measured following sample excitation with the 532 nm output from a frequency-doubled Spectra-Physics GCR-150-10 Nd:YAG laser (fwhm, ~8 ns) using a setup previously described.[20] The output from a 150 W Xe arc lamp (USHIO) powered by a PTI PS-220 power supply, pulsed with electronics built in-house, was focused onto the sample at 90° with respect to the laser beam The white light transmitted by the sample was collimated and focused onto the entrance slit of a Spex H-20 single monochromator (1200 gr/mm) and was detected utilizing a Hamamatsu R928 photomultiplier tube. For transient absorption signals above 600 nm either a 570 or 950 nm cutoff filter was placed in front of the monochromator to avoid detection of second-order grating reflections. The signal was digitized on a Tektronics 400 MHz oscilloscope (TDS 380), and the data were collected on a PowerMac 7600/132 (Apple) equipped with a National Instruments GPIB interface (NI-488.2) and a National Instruments data acquisition board (PCI-1200) and programmed with Labview 4.1 software. The timing of the triggering of the laser oscillator and Q-switch, the lamp pulser, and various shutters was accomplished using a digital delay generator (SRS DG535), whose action was coupled to the acquisition cycles of the computer through AND-gate circuitry. Attenuated scattered laser light yielded an overall instrument response function with fwhm = 12.5 ns. The samples used in all transient absorption experiments were subjected to three freeze−pump−thaw cycles or were bubbled with $N_2$ or Ar gas for 15 min immediately prior to each measurement.

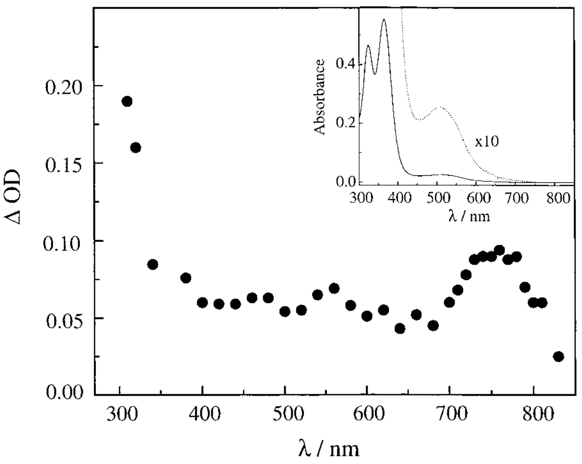

**Figure 2.** Transient absorption spectrum of 0.3 mM $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in $CH_3OH$ collected 500 ns after excitation ($\lambda_{exc}$ = 532 nm, ~10 mJ/pulse). The inset shows the ground-state electronic absorption spectrum of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in $CH_3OH$.

## Results and Discussion

**Emission and Time-Resolved Absorption.** No emission was observed from methanol solutions of $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) in the 500−1100 nm spectral region at room temperature using excitation wavelengths ranging from 300 to 600 nm. Placing the complexes in a quartz liquid nitrogen Dewar at 77 K in methanol or as solids did not result in any observed emission between 500 and 950 nm. To our knowledge, there have been no previous reports of emission from $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py).

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 time scale. Figure 2 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 excitation laser pulse (the ground-state electronic absorption spectrum is shown in the inset). The return of each transient signal at ~760 nm to the baseline ($\Delta$OD = 0) could be fit to a monoexponential decay with a lifetime of 5.0 $\mu$s. 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 $\mu$s) and in $CH_2Cl_2$ ($\tau$ = 4.6 $\mu$s). The transient absorption spectra of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = THF, py) complexes in methanol exhibit spectral profiles similar to that shown in Figure 2 with monoexponential lifetimes of 3.5 and 4.8 $\mu$s, 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 300−850 nm range. On the basis of 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 (60−600 $\mu$M) and excitation pulse energy (9−16 mJ/pulse). Plots of laser pulse energy vs transient signal intensity at 760 nm are consistent with a one-photon process. The time-resolved absorption spectral profiles and lifetimes of $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, $PPh_3$) remain unchanged when 355 nm excitation is used instead of 532 nm, and for a solution of a given concentration of each complex the intensity of the transient signal is proportional to the absorption at the excitation wavelength.

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The results described above indicate that the transient absorption signal arises from excitation of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) complexes and provide evidence as to the identity the observed transient. Many transient species observed upon excitation of metal complexes are known to arise from ligand-loss photochemistry.[21] Photochemical loss of an axial ligand is inconsistent with the insensitivity of the decay kinetics of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ in $CH_3OH$ or $CH_2Cl_2$ as solvents. Additionally, the spectra and decay characteristics of $Rh_2(O_2CCH_3)_4(L)_2$ (L = THF, $PPh_3$, py) complexes are very similar to that of the complex with L = $CH_3OH$ in methanol, although THF, $PPh_3$, and py are significantly less labile than $CH_3OH$.[22] 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 chelating ligand at a single Rh(II) center has also been ruled out because the addition of excess (0.6 M) $NaO_2CCH_3$ to a methanol solution of 200 $\mu$M $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ does not change the decay kinetics of the transient. Furthermore, the formation of a ground-state $Rh_2(\eta^2\text{-}O_2CCH_3)_3(\eta^1\text{-}O_2CCH_3)$ intermediate is inconsistent with its ability to undergo energy and electron transfer.

The transient absorption spectrum of each of the complexes in the series $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) exhibits a peak with a maximum at ~760 nm, as shown in Figure 2 for $Rh_2(O_2CCH_3)_4(PPh_3)_2$. 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 ($\epsilon = 249$ $M^{-1}$ $cm^{-1}$) for L = $H_2O$ and 775 nm ($\epsilon = 187$ $M^{-1}$ $cm^{-1}$) for L = $CH_3OH$,[18a,23b] which is not present in the absorption spectra of the corresponding neutral complexes. It might, therefore, be tempting to assign the peak at 750–760 nm in our transient spectra of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) complexes to photooxidation upon laser excitation. However, in $[Rh_2(O_2CEt_3)_4(PPh_3)_2]^+$ this transition is shifted to 538 nm,[18a] inconsistent with the 760 nm peak observed in the transient absorption spectrum (Figure 2). In addition, the broad absorption expected for the solvated electron at $\lambda > 700$ nm under $N_2$ is not observed and the decay kinetics of the transient at 760 nm are monoexponential, inconsistent with the second-order recombination of the oxidized $Rh_2$(II,III) complex with the photoejected electron. Furthermore, the lifetime of the transient is independent of initial concentration of the $Rh_2$(II,II) complex, of the laser light intensity, and of the solvent ($CH_2Cl_2$ and $CH_3OH$), all of which would affect the recombination kinetics of the oxidized $Rh_2(II,III)^+$ system with the solvated electron or other species in solution.

**Photoinduced Energy and Electron Transfer.** Excitation of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in methanol with 532 nm in the presence of perylene results in the quenching of the lifetime of the Rh(II) transient at 760 nm and in the production of a long-lived transient ($\tau \approx 50-100$ $\mu$s) with absorption centered at 485 nm. From the absorption maximum and lifetime, this long-lived transient can be assigned to the $^3\pi\pi^*$ excited state of perylene ($E_{00} = 1.30$ eV).[24,25] The triplet excited state of perylene results from energy transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ upon laser excitation. No transient signals were observed upon excitation with 532 nm of a solution containing only perylene. Unfortunatley, detailed kinetic measurements were complicated by subsequent triplet–triplet annhilation reactions of the perylene $^3\pi\pi^*$ excited state, which are known to result in the formation of the luminescent $^1\pi\pi^*$ of the molecule followed by reactions of the singlet, including the production of the perylene radical cation ($\lambda_{abs} = 537$ nm) and the radical anion ($\lambda_{abs} = 578$ nm).[25–28] The energy transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ to perylene conclusively shows that the $Rh_2$ transient species produced upon visible excitation with $\lambda_{abs} = 760$ nm is an excited state of the molecule. No energy transfer was observed in the presence of 9,10-diphenylanthracene ($Ph_2$-An) with $E_{00}(^3\pi\pi^*) = 1.77$ eV.[29]

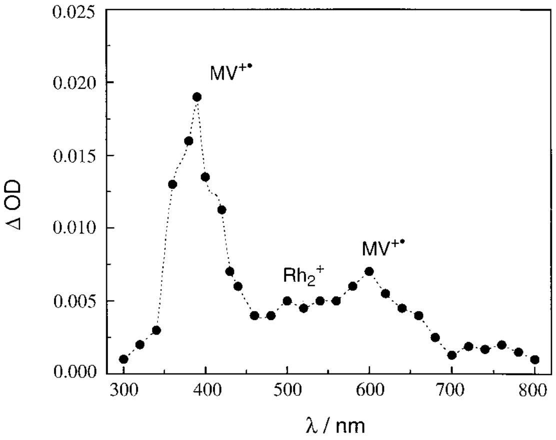

**Figure 3.** Transient absorption spectrum of 0.3 mM $Rh_2(O_2CCH_3)_4(PPh_3)_2$ in $CH_3OH$ in the presence of 5 mM $MV^{2+}\cdot 2BF_4^-$ ($\lambda_{exc}$ = 532 nm, ~10 mJ/pulse), collected 3.5 $\mu$s after excitation.

As shown in Figure 3, electron transfer to 4,4′-dimethyl viologen ($MV^{2+}$) is observed upon 532 nm excitation of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, where the absorption peaks of $MV^{+\bullet}$ at 395 and 605 nm are observed in the transient spectrum, as well as absorption at ~538 nm corresponding to $Rh_2(O_2CCH_3)_4(PPh_3)_2{}^+$.[18a] Stern–Volmer plots of $\tau_o/\tau$ vs $[MV^{2+}]$, where $\tau_o$ and $\tau$ 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) in methanol proceeds with a rate constant of $1.2 \times 10^6$ $M^{-1}$ $s^{-1}$.

From the oxidation potential of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ (+0.88 V vs NHE)[30] and the reduction potential of the acceptor $MV^{2+}$ (−0.46 V vs NHE),[31] a value of $E_{00} \geq 1.34$ eV can be estimated for the dirhodium complex. $Rh_2(O_2CCH_3)_4(PPh_3)_2$ is also quenched by $O_2$ ($E_{00}(^1\Delta_g) = 1.0$ eV)[32] in methanol with $k_q = 2 \times 10^8$ $M^{-1}$ $s^{-1}$. In contrast, 9,10-diphenylanthracene ($E_{1/2}(D^{+/0}) = +1.46$ V vs NHE, $E_{00}(^3\pi\pi^*) = 1.77$ eV)[27] or phenothiazine

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($E_{1/2}(D^{+/0}) = +0.45$ V vs NHE, $E_{00}(^3\pi\pi^*) = 2.62$ eV)[33,34] did not result in quenching of the $Rh_2(O_2CCH_3)_4(PPh_3)_2$ transient following 532 nm excitation through oxidation of the quencher or energy transfer. The observation of electron transfer is also consistent with the formation of an excited state of the $Rh_2(O_2CCH_3)_4(PPh_3)_2$ 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 and 1.77 eV.

Although a precise assignment of the electronic transitions observed in the spectrum of the excited state has not been made at this time, some important points are discussed below. The energies of the Rh−Rh $\sigma$ and $\sigma^*$ orbitals are profoundly affected by the $\sigma$-donor ability of the axial ligands.[17,18] This interaction results in different electron configuration for the oxidized $Rh_2(O_2CCH_3)_4(L)_2^+$ complexes with $H_2O$ and $PPh_3$ axial ligands, possessing $(\pi^*)^3$ and $(\sigma_{PPh3})^1$ HOMOs, respectively.[23] Notably, the transient spectra and lifetimes of the $Rh_2(O_2CCH_3)_4(L)_2$ (L = $CH_3OH$, THF, $PPh_3$, py) systems are relatively invariant to the choice of axial ligand. This observation allows us to rule out the participation of the Rh−Rh $\sigma$ and $\sigma^*$ orbitals in the transitions of the excited state. 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 $\pi^*(e_g) \rightarrow \sigma^*(a_{2u})$ transition;[2,3,13,16,35] thus, photoexcitation initially creates a hole in the $\pi^*$ orbital upon excitation. The transitions in the excited state of the complex may arise from metal-centered orbitals that do not possess $\sigma$ or $\sigma^*$ parentage or carboxylate orbitals to $\pi^*$, both of which are expected to be relatively independent of the axial ligands. The detailed assignment of the excited state is currently under investigation.

## Conclusions

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 (3.5−5.0 $\mu$s) assigned as an electronic excited state of the molecules. 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 perylene takes place to form the acceptors's $^3\pi\pi^*$ excited state. Electron transfer from $^*Rh_2(O_2CCH_3)_4(PPh_3)_2$ to 4,4′-$MV^{2+}$ and Cl−BQ occurs with quenching rate constants of $8.0 \times 10^6$ and $1.2 \times 10^6$ $M^{-1}$ $s^{-1}$ in methanol, respectively. A $k_q$ value of $2 \times 10^8$ $M^{-1}$ $s^{-1}$ 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 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 and 1.77 eV.

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