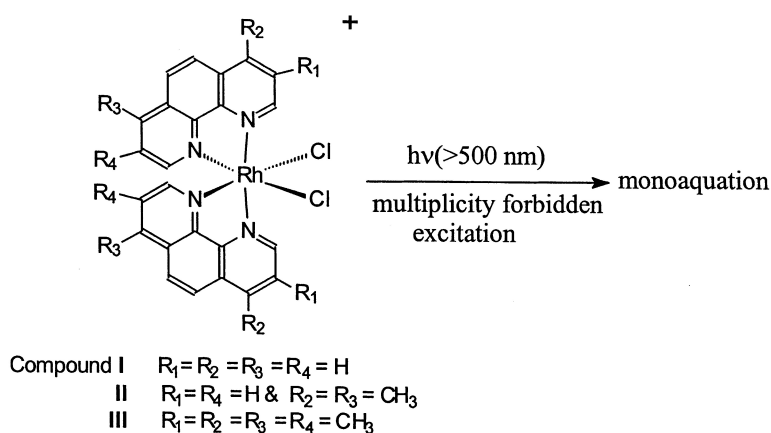Communication

Photoaquation of Methylated
cis-Dichlorobis(1,10-phenanthroline)rhodium(III)chloride Compounds
by Direct Population of a Photoactive Triplet Excited State

Devanesan Loganathan, Jorge H. Rodriguez, and Harry Morrison

Compound I $R_1 = R_2 = R_3 = R_4 = H$
II $R_1 = R_4 = H$ & $R_2 = R_3 = CH_3$
III $R_1 = R_2 = R_3 = R_4 = CH_3$

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Photoaquation of Methylated
cis-Dichlorobis(1,10-phenanthroline)rhodium(III)chloride Compounds by Direct Population of a Photoactive Triplet Excited State

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We have been interested in the photochemistry and photobiology of *cis*-dichlorobis(1,10-phenanthroline)rhodium(III)chloride, *cis*-Rh-$(phen)_2Cl_2^+$, and its analogues for some years.[1] The photochemistry of this family of compounds drew our attention because of its similarity to the thermal chemistry of the widely used cancer chemotherapeutic drug, *cis*-diamminedichloro platinum(II), *cis*-Platin. The rhodium complexes are chemically inert to aquation under thermal conditions in neutral aqueous media, but the chloride ligands are replaced sequentially by water upon UVA irradiation.[2,3] In such bis(phenanthroline)Rh(III) complexes, excitation with UVA light typically populates low-lying singlet ligand field states, the absorption for which occurs between 330 and 400 nm.[4] Intersystem crossing to the triplet manifold from the initially generated excited singlet states is highly efficient in these rhodium complexes,[5] and their photoreactivity is generally ascribed to their ligand field triplet states. *We now report that one can generate analogous photochemistry in two methylated analogues of cis-Rh(phen)₂Cl₂⁺, II and III, upon their direct excitation into the triplet manifold (i.e., with visible light > 500 nm).* To our knowledge, this is the first report of such ligand field photochemistry occurring by direct excitation into the triplet state of an octahedral rhodium(III) complex (Figure 1). It is also noteworthy that methyl substitution of the aromatic rings, as in **II** and **III**, increases the triplet photoreactivity of these complexes by 10-fold relative to the unsubstituted analogue, **I**. We are unaware of any prior reports of such a dramatic effect of ring methylation of aryl ligands on the ligand field triplet photochemistry of low spin d^6 transition metal complexes.

Aqueous solutions (3 mL, 0.1 mM) of the Rh complexes were irradiated for 8 h under argon using a 450 W Hanovia medium-pressure mercury lamp filtered through a uranium yellow glass (cutoff < 330 nm) and a 1.5 cm 0.5% (w/v) aqueous solution of $K_2Cr_2O_7$ (0% transmittance ≤ 500 nm). Photodestruction of the metal complexes was followed by HPLC analysis. Compound **I** was virtually unaffected by such long-wavelength excitation, but **II** and **III** showed measurable levels of photodestruction (6.1% and 9.3% loss, respectively). The enhanced visible-light reactivity caused by methylation of the phenanthroline rings reflects the measured quantum efficiencies of the photodestruction of these compounds at 311 nm (where precise extinction coefficients are known): **III** (0.20) ≈ **II** (0.18) ≫ **I** (0.02).[6]

As we anticipated, the major product of the long-wavelength photochemistry is the corresponding monoaquation product.[1,3] This was confirmed by LC/MS-ESI analysis of the photolyzate, which in each case provided a molecular ion for the major peak corresponding to the monoaquation product. ^{1}H NMR spectral analyses of the reactions in D_2O are consistent with this assignment. The loss of symmetry upon replacement of a chloride by water in **II** leads to a change from two to four singlets for the methyl
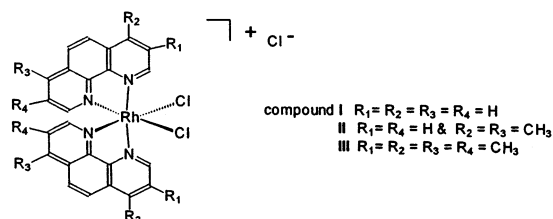
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Figure 1. Structures of *cis*-Rh(phen)₂Cl₂ complexes.

compound I R₁ = R₂ = R₃ = R₄ = H
          II R₁ = R₄ = H & R₂ = R₃ = CH₃
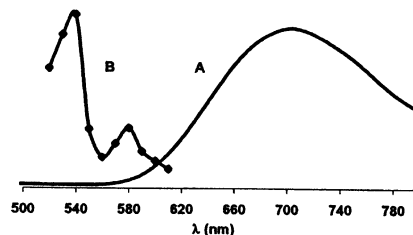   III R₁ = R₂ = R₃ = R₄ = CH₃

Figure 2. Normalized spectra for compound **III**. A = Phosphorescence spectrum at 77 K in a methanol/water glass; B = action spectrum for photoaquation at room temperature with >500 nm light. The points at 540, 580, and 600 nm are the average of three runs; other points are the average of two runs. The $S_0 \rightarrow S_n$ absorption spectrum ends at λ < 500 nm.

resonances, and from one to two doublets for the downfield phenanthroline hydrogen closest to the chloride. Likewise, in the photolysis of **III**, the four methyl singlets double to eight, and the single downfield phen-H singlet becomes two singlets.

To more specifically identify the transition responsible for the visible light photochemistry, we determined an "action spectrum" for the photoaquation in compound **III** using dye lasers emitting between 520 and 610 nm.[7] The percent photoaquation, normalized for photons incident on the laser cell at each wavelength, is shown in Figure 2 and indicates two maxima at ca. 540 and 580 nm.[8] The transition at 580 nm matches well with the observed onset of phosphorescence emission at 77 K from **III**, also shown in Figure 2.[9] The phosphorescence onset for **III** at ca. 600 nm is consistent with a similar onset reported for **I**.[4] In the absence of vibronic fine structure, one can use the onset of phosphorescence to approximate the energy of the 0,0 band of the singlet to triplet transition. Of course, our assumption here is but part of a set of arguments that include the action spectrum and the theoretical analysis. We were unsuccessful in observing UV−vis absorption bands for these complexes in this region using a 10 cm path length cell and a saturated aqueous solution (∼1.5 mM).

Time-dependent density functional calculations (TD-DFT)[10] were carried out on **I** and **III**. The lowest energy singlet to singlet excitations were calculated at 465 and 461 nm, both well to the blue of the wavelengths used for photochemical excitation in this study. The singlet to singlet excitations with largest oscillator strength were calculated at 256 and 291 nm, respectively. The

calculated energies and intensities in the gas phase are in fair quantitative and qualitative agreement with the experimental absorption spectra recorded in water. Formally forbidden singlet to triplet excitations were also calculated for **I** and **III**. Within the framework of TD-DFT, all such excitations yield a zero oscillator strength, and no absorption intensities are predicted. The lowest energy singlet to triplet excitations were calculated at 557 and 554 nm for **I** and **III**, respectively. These latter values suggest that one might expect to initiate singlet to triplet excitation using wavelengths of light $\geq$ ca. 550 nm.

One is left to explain why methylation of the phenanthroline rings enhances the photoaquation so markedly that reactivity is observed even upon direct singlet to triplet excitation. We do *not* believe that the answer lies in any significant rearrangement of metal and ligand centered excited states. Compound **I** exhibits a low intensity ($\epsilon \leq 100$) shoulder on the red edge (ca. 385 nm) of its UVA absorption that has been assigned to a $^1T_1 \leftarrow {}^1A_1$ transition that populates a lowest-lying d−d state.[11] Likewise, the lowest-lying triplet for **I** has been assigned as a d−d state on the basis of the broad, structureless nature of its phosphorescence (λ_{max} at 710 nm) and the emission's insensitivity to solvent environment, its lack of vibrational fine structure, and its relatively short lifetime (47.3 μs at 77 K).[4,11] In the methylated analogues, **II** and **III**, the ligand absorption maxima are only slightly red-shifted (7−9 nm) relative to **I**, and the d−d bands occur at wavelengths virtually identical to that in the parent complex. Both **II** and **III** show phosphorescence with a maximum at ca. 710 nm (77 K) that is Gaussian shaped and in appearance quite similar to the emission from **I**. Others have observed that the d−d triplet state energy for K[Rh(phen)Cl$_4$] is also relatively insensitive to the presence of phenanthroline methyl substituents.[12] We therefore assign the excited state directly populated by long-wavelength visible light to the metal centered $^3T_1$ state.[8] Such transitions have been previously reported for *trans*-[Rh(en)$_2$Cl$_2$]Cl at ca. 469 nm ($\epsilon \approx$ 1.5) and for *trans*-[Rh(py)$_4$Cl$_2$]Cl at ca. 465 nm ($\epsilon \approx$ 3) as weak inflections in the low energy region of their absorption spectra.[4]

If the state assignment for the lowest-lying triplet remains unaltered by methyl substitution on the phenanthroline rings, why then is visible light-initiated photochemistry observed for compounds **II** and **III** and not for **I**? It is likely that the extinction coefficients for the singlet−triplet transitions in this series are not markedly affected by the methylation because the extinction coefficients for the singlet−singlet ligand field transitions in all of these complexes are virtually the same. We believe the answer lies in the 10-fold greater quantum efficiencies for photoaquation observed at 311 nm. Because intersystem crossing is likely to be virtually complete in all three rhodium complexes,[5] the enhanced quantum efficiencies of the methylated analogues must be due to an increased rate of aquation of their metal-centered triplet states. A dissociation/addition mechanism is generally accepted as being responsible for the substitution chemistry associated with a hexa-coordinated Rh(III) ligand field triplet.[13] The dissociation step is due to the promotion of an electron from the t$_{2g}$ orbital to the e$_g$ orbital, which leads to significant weakening of the metal ligand bonds.[14] The increased reactivity exhibited by **II** and **III** may be attributed to an increase in σ-donation from the methylated phen ligands to the Rh,[15] which should markedly stabilize the penta-coordinate species formed by the dissociation of the labile Cl$^-$ and/ or the transition state leading to it. In fact, there is evidence that

the reactivity of **II** and **III** is enhanced *in the ground state* in a similar fashion. Although all of these complexes are extremely stable to dark thermal aquation, they can be hydrolyzed by base, and we have observed that such thermal hydrolysis at 80 °C with 10% NaOH follows the same trend as that of photoaquation, that is, **III** $\approx$ **II** > **I**.

We are currently exploring the incorporation of this visible light initiated triplet photochemistry into our ongoing studies of the potential use of bisphenanthroline rhodium(III) complexes as phototoxic agents.[1]

Supporting Information Available: ^{1}H NMR (DMSO-d_6), ^{13}C NMR (DMSO-d_6), HRMS(ESI) for compounds **II** and **III**, the LC/MS traces for the major products of the photolyzate of **II** and **III**, and the ^{1}H NMR spectra of the photolysis reaction solutions of **II** and **III** in D$_2$O. Absorption and low-temperature emission spectra of compounds **II** and **III**. Calculated UV−visible spectra of compounds **I** and **III** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The laser power was maintained below 52 mW at all wavelengths. Studies at 580 nm (89 and 46 mW) and at 540 nm (61 and 38 mW) showed the products formed are independent of laser power.
(8) The apparent fine structure of the action spectrum may be due to splitting of the $^3T_{1g}$ state due to the lower (D_2) symmetry of **III**, or to the resolution of the $^3T_{1g}$ and $^3T_{2g}$ states. For a proposal of two reactive LF triplets in halopentaammine Rh(III) complexes, see: Kelly, T. L.; Endicott, J. F. *J. Phys. Chem.* **1972**, *76*, 1937.
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