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# Ultrafast Ligand Exchange: Detection of a Pentacoordinate Ru(II) Intermediate and Product Formation

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Photoinduced ligand loss, and in some cases isomerization, represents the initial step in reactions with potential applications that include photodynamic therapy (PDT),[1] solar energy conversion,[2] molecular switches,[3] and C−H activation.[4] Transition metal complexes with monodentate ligands covalently coordinate to DNA upon irradiation with visible light, which leads to an increase in cytotoxicity greater than that of the approved PDT agent.[1] Some of the C−H activation catalysts have been substituted with photolabile CO ligands, such that the ligand-loss and subsequent formation of products can be followed using time-resolved IR spectroscopy.[4−6] For most systems that lack an IR handle, however, the photoinduced ligand exchange kinetics remain unknown. The present work describes the direct measurement of ligand exchange kinetics on the picosecond time scale.

Steady-state irradiation of *cis*-$[Ru(bpy)_2(CH_3CN)_2]Cl_2$, [**1**]$Cl_2$, in water results in the stepwise replacement of each $CH_3CN$ ligand with $H_2O$. The formation of the monoaqua intermediate, *cis*-$[Ru(bpy)_2(CH_3CN)(H_2O)]^{2+}$ (**2**), is evident during the photolysis at early times by the appearance of a maximum at ∼458 nm (Figure S1, Supporting Information). Power dependence studies reveal that the formation of the bis-aqua product, *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ (**3**), from **1** is a two-photon process, such that a second photon is required for the release of $CH_3CN$ from **2** to generate **3**. The quantum yield for the formation of **3** is significantly higher than that observed for other Ru(II) complexes; the values are 0.38 (350 nm), 0.21 (400 nm), and 0.22 (450 nm). Owing to the high photoaquation quantum yield of **1**, transient absorption can be used to measure the ligand exchange kinetics through the direct detection of photogenerated intermediate(s).

The transient absorption spectra of 890 $\mu$M [**1**]$Cl_2$ in $H_2O$ following ultrafast excitation ($\lambda_{exc}$ = 310 nm, fwhm ∼300 fs) in a flow cell are shown in Figure 1. At early times typical features of the $^3$MLCT excited-state are observed (Figure 1a), including absorption with a maximum at 363 nm corresponding to $bpy^-$ and a broad absorption at 500 nm, along with bleaching of the ground-state absorption at 427 nm.[7] The decrease in intensity of the broad feature at 500 nm can be fitted to a biexponential decay of 2 and 5 ps at early times, resulting in the spectrum with a broad absorption at $\lambda$ > 475 nm and a small peak at 465 nm at $t$ = 10 ps (Figure 1). These early spectral changes in Ru(II) complexes have been previously attributed to intersystem crossing and internal conversion, as well as vibrational cooling.[3,6b,7] Therefore, significant population of the $^3$MLCT excited-state is expected at $t$ = 10 ps (Figure 1). Indeed, the decay of the bleach at 427 nm and the $bpy^-$ signal at 363 nm are small from 0.5 to 10 ps, consistent with population of the $^3$MLCT at 10 ps.

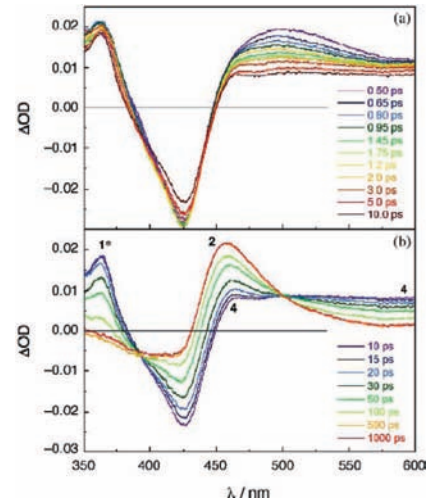


***Figure 1.*** Transient absorption spectra of **1** in $H_2O$ collected at (a) 0.5 to 10 ps and (b) 10 ps to 1 ns following excitation ($\lambda_{exc}$ = 310 nm, fwhm ∼ 300 fs).

After 10 ps, a quasi-isosbestic point is observed at 500 nm (Figure 1b), characterized by a decrease in the absorption of the signal at $\lambda$ > 500 nm and an increase in absorption with a maximum at 458 nm, known to correspond to the one-photon monoaqua complex **2** (Figure S1, Supporting Information). Recovery of the bleach signal and decrease of the $bpy^-$ absorption at 363 nm are also observed from 10 to 300 ps, after which time no additional spectral changes are apparent. Owing to the presence of the isosbestic point at 500 nm, the absorption features at $\lambda$ > 500 nm in the spectrum collected at 10 ps are attributed mostly to the pentacoordinate intermediate $[Ru(bpy)_2(CH_3CN)]^{2+}$ (**4**), with small contributions from the vibrationally cooled $^3$MLCT. At 10 ps, the absorption of the $^3$MLCT state is still strong at 363 nm, and decays monoexponetially with $\tau$ = 52 ps. The recovery of the bleach signal is biexponential with 50 and 77 ps components. The 50 ps component is assigned to the decay of the $^3$MLCT excited-state to regenerate the ground state ($^1$GS), similar to data in other solvents and for a related complex.[3] The formation of **2** from **4** takes place with $\tau$ = 77 ps. These processes are shown schematically in Figure 2a.

At other wavelengths, ∼18 ps and ∼30 ps components are also measured following excitation of **1** in water. In order to make the correct assignments of these components, the ultrafast transient absorption spectra of the $PF_6^-$ salt of **1** were also collected in $CH_3CN$ (Figure S2, Supporting Information) and in $CH_2Cl_2$. In both solvents, early components of 2 and 6 ps are observed, similar to the early kinetics in water. The spectral features at 10 ps are similar to those in water at the same delay time, consistent with the fast

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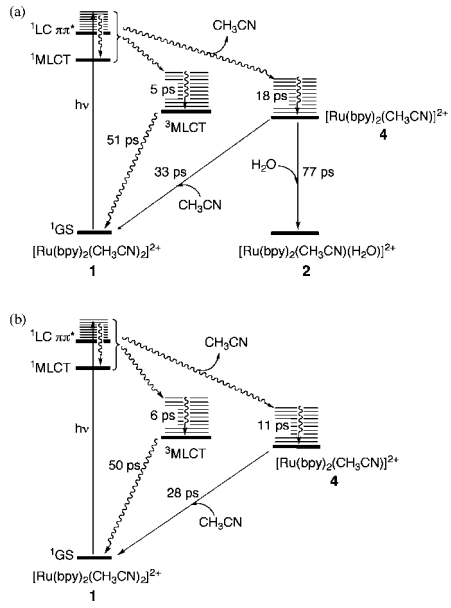


***Figure 2.*** Average ultrafast kinetics of **1** showing the formation and reactivity of **4** in (a) $H_2O$ and (b) $CH_3CN$.

formation of **4**. The signal from the $^3$MLCT at 370 nm decays with $\tau = 50$ ps and the bleach recovery can be fitted to a biexponential decay with $\tau = 28$ ps and $\tau = 50$ ps. At 600 nm, the decay of **4** is biexponential with 11 and 28 ps components. The latter is consistent with ligand recombination to regenerate **1**. As is the case in $H_2O$ (Figure 1), the signals from the $^3$MLCT (370 nm) and from **4** (465 and 600 nm) are present at $t = 2$ ps, therefore, the ligand-loss must take place before this time, as schematically depicted in Figure 2b. Since shifts in these peaks are not evident from 2−10 ps, the 11 ps component has been assigned as vibrational cooling of **4**, although a molecular rearrangement of the five-coordinate species cannot be ruled out. By analogy, the vibrational cooling of **4** in $H_2O$ takes place with $\tau = 18$ ps. Similar spectral features and decays were measured in $CH_3CN$ and $CH_2Cl_2$, showing that ligand recombination takes place following the initial separation within the solvent cage.

Steady-state photolysis experiments provide additional support for the ligand-loss and recombination of **1** in $CH_3CN$. The $^1$H NMR spectrum of 10 mM of the $PF_6$ salt of **1** in $CD_3CN$ exhibits a singlet at $\delta = 2.26$ ppm corresponding to the two bound $CH_3CN$ ligands (Figure S3, Supporting Information). A decrease in intensity of this peak is observed upon photolysis ($\lambda_{irr} \geq 420$ nm) over a period of 20 min, with concomitant increase in the free $CH_3CN$ peak at $\delta = 1.97$ ppm (Figure S3, Supporting Information). These results indicate that, indeed, photoinduced ligand-loss and recombination takes place in **1** in $CH_3CN$, as depicted in Figure 2b. Since the kinetics of this ligand exchange are fast, bimolecular reactivity by the five-coordinate intermediate in $CH_3CN$, with $\tau = 28$ ps, is not expected to take place at low concentrations. Indeed, photolysis of 25 $\mu$M **1** in the presence of 25 $\mu$M bpy do not result in changes in the absorption spectrum in $CH_3CN$ ($\lambda_{irr} \geq 420$ nm, 2.5 h), and no emission from $[Ru(bpy)_3]^{2+}$ was detected ($\lambda_{exc} = 450$ nm).

The decay of the intermediate **4** in water, which absorbs at 600 nm, can be fitted to a biexponential function with lifetimes of 34 and 80 ps. The former is similar to the 28 ps lifetime measured for **1** in $CH_3CN$ and $CH_2Cl_2$, and is assigned to ligand recombination within the solvent cage to regenerate **1** (Figure 2a).

The small peak at 10 ps with maximum at 465 nm assigned to the MLCT absorption of the five-coordinate intermediate, **4**, which blue-shifts to 458 nm upon coordination by $H_2O$ to generate **2**. This shift provides support for the assignment, since ligation is expected to increase the ligand-field splitting of the metal. The assignment is consistent with a Ru(II) species, and not Ru(III).

It should be noted that ligand loss and recombination in the fs to ps timescales has been previously reported for various complexes containing CO ligands.[6] In the related Ru(II) complexes, *trans*-(X,X)-$[Ru(X)_2(CO)_2(bpy)]$, where X = Cl, Br, and I, CO substitution with $CH_3CN$ takes place in 13−55 ps from the five-coordinate intermediate.[6b] In *trans*-(X,X)-$[Ru(X)_2(CO)_2(bpy)]$, as well as in $Cr(CO)_4(bpy)$ and fac-$[Re(bpy)(CO)_3Cl]$, ligand loss is believed to take place from the initially populated singlet excited states, such that ligand loss competes with the population of the $^3$MLCT. In the case of $[CpIr(CO)_2]$ (Cp = cyclopentadiene), ligand loss and C−H activation are complete within 2 ps, and regeneration of the starting material through the population of an excited-state and another intermediate requires 40 ps.[4] The results shown here are similar to those of other transition metal complexes.

The present results demonstrate the competition between the population of the $^3$MLCT excited-state and ligand loss on the fs to ps timescales. The data indicate that the exchange with a ligand L (L = py, DNA bases) upon irradiation of **1** in $H_2O$ to generate $[Ru(bpy)_2(CH_3CN)(L)]^{2+}$ must proceed through the monoaqua complex, **2**, since the lifetime of the five-coordinate intermediate (**4**) is too short to permit bimolecular reactivity at low concentrations. These data are useful for the future design of new systems with improved properties and in the interpretation of data on related systems.

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**Supporting Information Available:** Synthesis, experimental setup, ultrafast spectra in $CH_3CN$, selected fits to decays, and $^1$H NMR spectra in $CD_3CN$. This material is available free of charge via the Internet at http://pubs.acs.org.

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