# Excited State Dynamics and Isomerization in Ruthenium Sulfoxide Complexes

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Albert W. King, Lei Wang, and Jeffrey J. Rack*

Nanoscale and Quantum Phenomena Institute, Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, United States

**CONSPECTUS:** Molecular photochromic compounds are those that interconvert between two isomeric forms with light. The two isomeric forms display distinct electronic and molecular structures and must not be in equilibrium with one another. These light-activated molecular switch compounds have found wide application in areas of study ranging from chemical biology to materials science, where conversion from one isomeric form to another by light prompts a response in the environment (e.g., protein or polymeric material). Certain ruthenium and osmium polypyridine sulfoxide complexes are photochromic. The mode of action is a phototriggered isomerization of the sulfoxide from S- to O-bonded. The change in ligation drastically alters both the spectroscopic and electrochemical properties of the metal complex. Our laboratory has pioneered the preparation and study of these complexes. In particular, we have applied femtosecond pump−probe spectroscopy to reveal excited state details of the isomerization mechanism. The data from numerous complexes allowed us to predict that the isomerization was nonadiabatic in nature, defined as occurring from a S-bonded triplet excited state (primarily metal-to-ligand charge transfer in character) to an O-bonded singlet ground state potential energy surface. This prediction was corroborated by high-level density functional theory calculations. An intriguing aspect of this reactivity is the coupling of nuclear motion to the electronic wave function and how this coupling affects motions productive for isomerization.

In an effort to learn more about this coupling, we designed a project to examine phototriggered isomerization in bis-sulfoxide complexes. The goal of these studies was to determine whether certain complexes could be designed in which a single photon excitation event would prompt two sulfoxide isomerizations. We employed chelating sulfoxides in this study and found that both the nature of the chelate ring and the R group on the sulfoxide affect the photochemical reactivity. For example, this reactivity may be tuned such that two sulfoxide ligands isomerize sequentially following two successive excitations or that two sulfoxide ligands isomerize following a single excitation. This Account explains our understanding to date of this photochemistry.
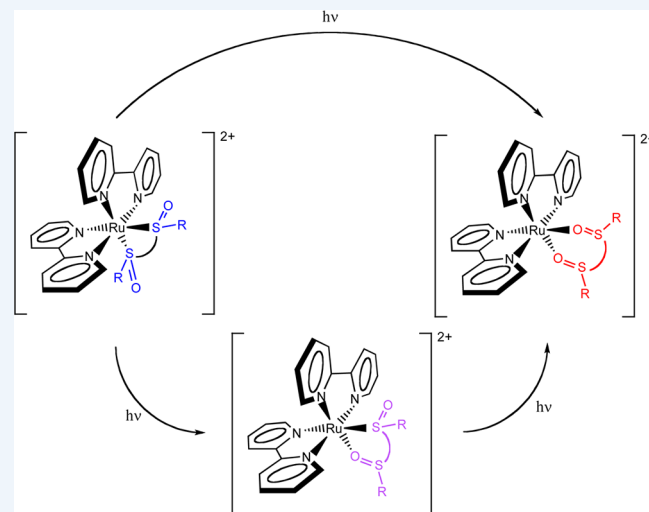
## INTRODUCTION

Photochromic compounds and complexes are light-activated molecular switches that form a subset of a larger class of materials termed molecular machines.[1,2] Molecular photochromism is simply defined as conversion of one isomer to another isomer with light.[3] The two isomeric forms must not be in equilibrium with one another and must exhibit intrinsically disparate electronic and molecular structures. One isomer is thus metastable on the ground state potential energy surface and will always revert to the lowest energy isomer thermally. There are examples of photochromic compounds in which the metastable state is kinetically trapped at room temperature. Subsumed within the photochemical

reaction are complicated details regarding energy conversion (photonic to potential) and vibronic and kinematic (mechanical) coupling in the excited state. The objective of this Account is to describe efforts to date in characterizing photochromic ruthenium and osmium sulfoxide complexes. These activities primarily include ultrafast visible pump probe spectroscopy to investigate excited state reactivity. Through a combination of spectroscopy, electrochemistry, and synthetic modification, we have sought to identify the key features of the isomerization mechanism exhibited by these compounds. Beyond the

optimization of this class of compounds for applications in information storage (holography), and solar thermal energy storage, the theoretical insights derived from this work impact the larger field of inorganic photochemistry, where excited state reactivity including ligand substitution remains important and topical in fields ranging from phototherapeutics to photocatalysis.

## ■ CHEMICAL STRUCTURE AND ISOMERIZATION PRINCIPLES

The basic structure of photochromic transition metal sulfoxide complexes requires a central ruthenium or osmium ion in the +2 oxidation state, a monodentate or bidentate sulfoxide ligand, and a ligand with low-lying, accessible $\pi^*$ orbitals for charge transfer that will trigger sulfoxide isomerization. The remaining coordination site(s) may be occupied by any ligand to tune the spectrochemical properties of the metal complex. We have investigated two primary structures (Figure 1): one class based
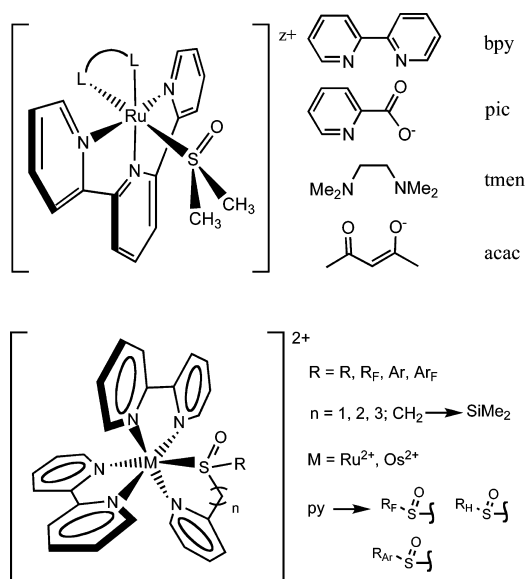


**Figure 1.** Bond line drawing of $[Ru(tpy)]^{2+}$ class (top) and $[Ru(bpy)_2]^{2+}$ class (bottom) of photochromic compounds. For the $[Ru(bpy)_2]^{2+}$ (and $[Os(bpy)_2]^{2+}$) class, the R group, the number and type of atoms in the chelate ring, and the second binding group (pyridine replaced with sulfoxide) may be optionally substituted.

on $[Ru(tpy)]^{2+}$ (tpy is 2,2′:6′,2″-terpyridine) with dimethyl sulfoxide and a variable bidentate ligand, and a second class incorporating chelating sulfoxide ligands on $[Ru(bpy)_2]^{2+}$ (bpy is 2,2′-bipyridine). Sulfoxide isomerization on $[Ru(tpy)]^{2+}$ proceeds by an adiabatic mechanism along the $^3MLCT$ (metal-to-ligand charge transfer) surface and has been reviewed previously.[4] In contrast, isomerization of sulfoxides on $[Ru(bpy)_2]^{2+}$ occurs in a nonadiabatic fashion with wide variability in temporal and spectroscopic response. These latter complexes are the focus of this Account, with a specific interest in bis-sulfoxide complexes. Also included are certain studies of sulfoxide isomerization on $[Os(bpy)_2]^{2+}$.

The creation of photochromic complexes based on sulfoxide isomerization on $Ru^{2+}$ or $Os^{2+}$ evolved from electrochemical studies of $[Ru(NH_3)_5(dmso)]^{2+}$, where Taube modeled the cyclic voltammogram obtained from this complex with an ECEC (electrochemical−chemical, electrochemical−chemical) mechanism.[5] Briefly, oxidation (electrochemical) of $Ru^{2+}$ to

form $Ru^{3+}$ prompted spontaneous isomerization (chemical) of the ground state S-bonded isomer to produce the O-bonded isomer. Subsequent reduction (electrochemical) of O-bonded $Ru^{3+}$ to $Ru^{2+}$ at a different potential induced spontaneous isomerization (chemical) to return to the original ground state $Ru^{2+}$ S-bonded isomer. Both isomerization reactions were intramolecular. We formed the structures depicted in Figure 1 in order to test whether the oxidized metal ion ($Ru^{3+}$, $Os^{3+}$) in heteroleptic polypyridine sulfoxide complexes formed from MLCT photoexcitation would trigger sulfoxide isomerization. This excited state is characterized by a formally reduced bpy ligand (bpy$^-$) and oxidized metal center ($Ru^{3+}$) and is comparable to the electrochemical oxidation product. Results from a number of laboratories show that this is true.[6−9]

Shown in Figure 2 is a simple depiction of molecular photochromism with hypothetical A and B isomers. Conversion
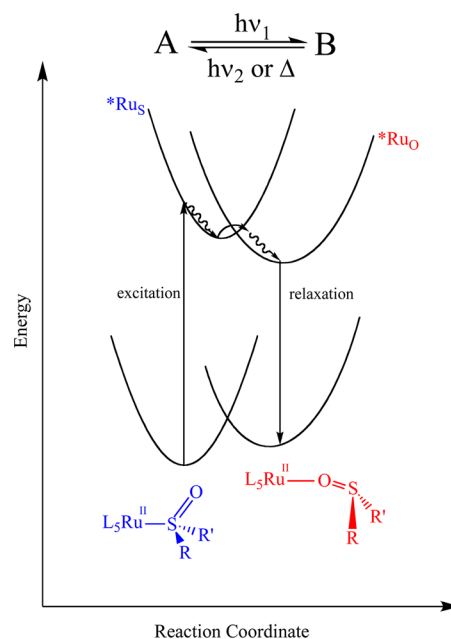


**Figure 2.** Four level diagram depicting S-bonded ground state and O-bonded metastable state and one excited state for each isomer.

of A to B occurs with one wavelength ($h\nu_1$), whereas conversion from B to A may occur either thermally or photochemically ($h\nu_2$). This photochemical reactivity is also represented in the four-level diagram in Figure 2. Here, conversion of the S-bonded sulfoxide (A isomer) to the O-bonded sulfoxide (B isomer) along the ground state potential energy surface is endergonic. However, MLCT excitation promotes the molecule onto the MLCT potential energy surface, and now isomerization is exergonic yielding an O-bonded $Ru^{2+}$ isomer. The O-bonded isomer is metastable on the ground state potential energy surface and will revert adiabatically to the S-bonded isomer. The dynamics of this reversion are determined by the activation barrier. The diagram in Figure 2 is a great oversimplification, since it only shows four states.[10] In actuality, there is no requirement that isomerization occurs on the excited state potential energy surface prior to relaxation or that isomerization is an activated process, as is depicted here. Nevertheless, this diagram does provide a construct in which to think about how synthetic modifications will alter the excited state reactivity.

Photochemical conversion of metastable O-bonded $Ru^{2+}$ to S-bonded $Ru^{2+}$ is not common. The diagram in Figure 2 neatly demonstrates why. Excitation of O-bonded $Ru^{2+}$ yields a MLCT excited state. However, for the curves depicted here, isomerization is an endergonic process and is thus disfavored, resulting in decay back to the O-bonded $Ru^{2+}$ ground state. The diagram in Figure 2 is not representative for structures that feature photochemical conversion of the O-bonded isomer to the S-bonded isomer. In those cases, the O-bonded excited state potential energy surface is not necessarily lower than the corresponding S-bonded surface. Those examples also indicate the presence of separate S → O and O → S isomerization pathways.

## PROPOSED MECHANISM FOR PHOTOTRIGGERED ISOMERIZATION

Phototriggered isomerization is a special case of photoinduced ligand substitution. For ruthenium polypyridine complexes (e.g., $[Ru(bpy)_3]^{2+}$), the basic model for such reactions has evolved over decades of work by many researchers.[11−13] In aggregate, for complexes with lowest energy $^3$MLCT excited states, ligand substitution occurs through thermal population of the formally antibonding Ru−L d$\sigma^*$ (e$_g$ set comprising $d_{x^2−y^2}$ and $d_{z^2}$ in $O_h$ symmetry) orbitals, also known as the metal-centered (MC) or ligand field (LF) states. The MC or LF states are higher in energy than the lowest energy MLCT state. For monodentate ligands, population of these $\sigma$-antibonding orbitals from the MLCT state prompts substitution on an ultrafast time scale, though chelating ligands may also be exchanged.[14,15] In contrast, ground state (dark) ligand substitution on $Ru^{2+}$ or $Os^{2+}$ occurs on a much longer time scale (seconds to minutes to hours). The energy gap between MLCT and LF states is important in determining excited state reactivity, and many strategies to tune this gap have emerged.[16,17] Moreover, quantum yields of emission (and substitution) are particularly sensitive to the magnitude of the energy gap. For $[Ru(bpy)_3]^{2+}$ and many of its derivatives, the emission quantum yield increases with a decrease in temperature. This is interpreted as thermal isolation of the emissive MLCT state from the nonemissive LF states. Recently, the role of strain in photoinduced ligand substitution has been investigated.[18] In phototriggered sulfoxide isomerizations, the reaction is intramolecular, but the relative energetics of the MLCT and LF states remain influential in the earliest steps of the reaction.

In ruthenium polypyridine sulfoxide complexes, the lowest energy MLCT absorption maxima and $Ru^{3+/2+}$ reduction potentials are typically shifted to higher energy relative to ruthenium polypyridine complexes absent a sulfoxide ligand. For example, prototypical $[Ru(bpy)_3]^{2+}$ features an absorption maximum ($\lambda_{max}$) at 452 nm and a formal reduction potential ($E^{\circ\prime}$) of 1.23 V vs NHE. In comparison, $[Ru(bpy)_2(dmso)_2]^{2+}$ (dmso is dimethyl sulfoxide) exhibits $\lambda_{max}$ at 355 nm and $E^{\circ\prime}$ of >2.4 V vs NHE.[19] A second, valuable comparison is $[Ru(bpy)_2(py)_2]^{2+}$ (py is pyridine; $\lambda_{max}$ of 455 nm and $E^{\circ\prime}$ of 1.24 V vs SCE)[20] with $[Ru(bpy)_2(py)(dmso)]^{2+}$ ($\lambda_{max}$ of 400 nm and $E^{\circ\prime}$ ~1.7 V vs SCE).[21,22] These data are indicative of Ru d$\pi$-stabilization (t$_{2g}$ set comprising $d_{xz}$, $d_{yz}$, and $d_{xy}$ in $O_h$ symmetry) by the sulfoxide relative to bipyridine or pyridine. In addition, metal sulfoxide (Ru−S) bond distances are typically shorter than their corresponding metal thioether bond distances, a correlation consistent with the sulfoxide acting as a $\pi$-acid or engaging in $\pi$-backbonding from $Ru^{2+}$ to S=O

$\pi^*$.[23] There is simply no reasonable $\sigma$-bonding argument to explain the correlated shift in the absorption spectra and electrochemical data relative to $[Ru(bpy)_3]^{2+}$. Such stabilization suggests that the d$\pi$ HOMO orbital set contains both Ru and S character. One then also expects the LF states to be much higher in energy in ruthenium sulfoxide complexes than in their pyridine or bipyridine counterparts. This assertion is supported by DFT calculations.[24−27]

Electronic spectral data support a large nuclear distortion (or structural rearrangement) between ground state and $^3$MLCT structures. We examined the absorption and emission spectra of a family of $[Ru(bpy)_2(OSOR)]^+$ complexes, where OSO is an optionally substituted alkyl- or aryl-2-sulfinylbenzoate, focusing on $[Ru(bpy)_2(OSOBnF_5)]^+$ (OSOBnF$_5$ is 2-pentafluorobenzylsulfinylbenzoate) in comparison with $[Ru(bpy)_3]^{2+}$.[28] Shown in Figure 3 is a plot of the normalized room temperature
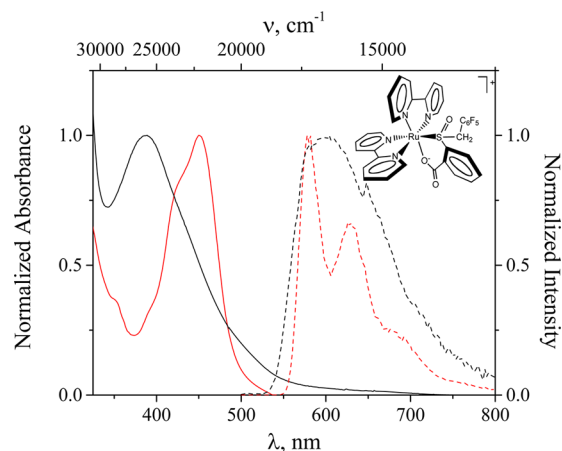


**Figure 3.** UV−visible (solid, methanol solution) and emission (dashed, 77 K 4:1 MeOH/EtOH glass) spectra of $[Ru(bpy)_2(OSOBnF_5)](PF_6)$ (black) and $[Ru(bpy)_3](PF_6)_2$ (red). The chemical structure is depicted as an inset. Adapted with permission from ref 28. Copyright 2010 American Chemical Society.

absorbance and 77 K emission spectra for these two complexes. It is readily apparent from the absorption profiles that the ruthenium sulfoxide complex exhibits a much broader fwhm (full width at half-maximum), which we estimated to be 7250 cm$^{-1}$. This is significantly broader than that observed for $[Ru(bpy)_3]^{2+}$ with fwhm of 3550 cm$^{-1}$. It is obvious that while the absorption maximum for the sulfoxide complex is substantially blue-shifted relative to that of $[Ru(bpy)_3]^{2+}$, the emission maxima are similar. The Stokes' shifts are found to be 8290 and 6000 cm$^{-1}$ for $[Ru(bpy)_2(OSOBnF_5)]^+$ and $[Ru(bpy)_3]^{2+}$, respectively. Such data demonstrate a large nuclear distortion or structural displacement between the equilibrium geometries of ground state and excited state structures. These data are consistent with recent DFT calculations.[24,25]

The initial excited state formed by visible light irradiation of these complexes is comparable to the canonical MLCT model: a reduced polypyridine ligand and an oxidized metal ion center. Pump−probe measurements show a relatively narrow excited state absorption ranging from 360 to 390 nm, a broad excited state absorption maximum at $\lambda$ > 550 nm, and a ground state bleach or negative peak corresponding to the ground state MLCT absorption maximum. In general, these features are diagnostic of MLCT excited states.[29,30] The UV feature has
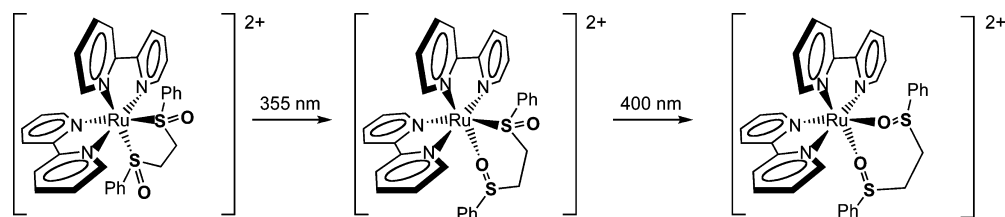
**Figure 4.** Bond line drawings of S,S-, S,O-, and O,O-[Ru(bpy)$_2$(bpSO)]$^{2+}$ and photochemical reactivity displaying sequential isomerizations of each sulfoxide ligand.

been previously assigned to a $\pi^* \rightarrow \pi^*$ absorption of the reduced bipyridine in the MLCT excited state, while the low energy feature has been ascribed to both a LMCT (ligand-to-metal charge transfer) transition from the unreduced bipyridine to Ru(III) and low energy $\pi^* \rightarrow \pi^*$ absorption of the reduced bipyridine.[29,30] Interestingly, the features we observe are not consistent with a purely lowest energy LF state. Such a transient would be characterized by the MLCT bleach feature but would not show excited state absorptions arising from a reduced bipyridine. This is nicely corroborated by a recent report by Hauser and co-workers.[31]

The consequence of S mixing in the HOMO is manifest immediately upon excitation. Promoting an electron from a bonding orbital with Ru and S character serves to weaken the Ru−S bond and accordingly sets in motion the initial steps of isomerization. Within the established framework of MLCT excited state dynamics, a $^3$MLCT is rapidly formed (<1 ps) from higher lying $^1$MLCT states with a greatly elongated Ru−S bond. Boggio-Pasqua and co-workers investigated [Ru-(bpy)$_2$(OSO)]$^+$ (OSO is 2-methylsulfinylbenzoate) and [Ru-(bpy)$_2$(dmso)$_2$]$^{2+}$ by DFT calculations and found that the $^3$MLCT state features a Ru−S bond that is ~0.5 Å longer than that found in the ground state![24,25] The result of the elongated Ru−S bond is profound. This partial decoordination of the ligand stabilizes (lowers in energy) the Ru−S $\sigma^*$ orbital(s), making them more accessible, and destabilizes (raises in energy) the $^3$MLCT state. The Ru$^{3+/2+}$ $E^{\circ\prime}$ is expected to shift to more positive potentials following partial ligand loss, because Ru will become more Lewis acidic. So, while the LF states are initially much higher in energy than the $^3$MLCT states in the ground state S-bonded isomer, *excitation prompts electronic changes bringing these states closer in energy and drives significant changes in molecular structure.*

There is a real question as to whether the lowest energy excited state is $^3$MLCT or LF (MC) in nature. DFT calculations of [Ru(bpy)$_2$(OSO)]$^+$ and [Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ predict a formal rearrangement of states such that the lowest energy excited state is metal-centered.[24,25,32] Spectroscopic data are not consistent with computational results. Time-resolved pump−probe spectroscopic data reveal electronic transitions that are only available in the $^3$MLCT excited state, as described above. Throughout the temporal evolution of the excited state dynamics and isomerization, the $^3$MLCT state appears to be lowest in energy. However, it must be noted that these complexes do not emit at room temperature but do emit at low temperature (77 K). This may be due to a close energetic ordering of nonemissive LF and emissive $^3$MLCT states or because the LF states are actually the lowest energy excited state at room temperature. Again, a lowest energy LF state is inconsistent with the room temperature pump−probe data. That emission is observed at 77 K provides strong evidence that

the $^3$MLCT is lowest energy at this temperature and is thermally isolated from the higher energy LF states.

We prefer a description in which the lowest energy excited state surface contains both LF and MLCT character, as opposed to two separate surfaces. It is from this surface that isomerization occurs. Based on the excited state behavior of [Ru(bpy)$_3$]$^{2+}$, we propose that the final steps of isomerization are facilitated by the LF states to produce both S-bonded and O-bonded structures on the ground state potential energy surface. Pump−probe measurements reveal some vibrational relaxation processes on the ground state O-bonded potential energy surface. Both DFT and pump−probe data indicate that isomerization occurs through a conical intersection between triplet excited state and singlet ground state surfaces, with (presumably) Ru−S stretching, Ru−O stretching, and sulfoxide twisting vibrations as critical modes coupling these surfaces.[25,26] Isomerization time constants are found in the range of 50 ps to 10 ns.

## ISOMERIZATION IN BIS-SULFOXIDE COMPLEXES

We have had a long-standing interest in ruthenium and osmium bis-sulfoxide complexes.[33−36] The goal of these studies is to learn which of the two sulfoxide ligands isomerizes first following light excitation and how to control such a reaction. Moreover, we are interested in finding examples where two isomerizations can be phototriggered subsequent to a single photon absorption. Below, we describe case studies of sequential single photon excitation leading to one isomerization and of single photon excitation prompting two isomerizations.

### One Photon Prompts One Isomerization

Shown in Figure 4 (left) is the structure of a bis-sulfoxide complex, [Ru(bpy)$_2$(bpSO)]$^{2+}$, where bpSO is 1,2-bis-(phenylsulfinyl)ethane.[37] The spectroscopic data of this compound are consistent with a model in which irradiation prompts sequential isomerization of each sulfoxide. Thus, the ground state S,S-isomer yields the S,O-isomer, which then produces the O,O-isomer subsequent to a second photon excitation. For example, bulk photolysis with 355 nm light shows loss of spectroscopic features associated with the S,S-isomer concomitant with a rise in features attributed to the S,O-isomer. Continued irradiation shows loss of these features with a corresponding rise in features assigned to the O,O-isomer. Indeed, there are two sets of isosbestic points connecting these transitions between isomers. The spectral changes are thermally reversible, taking a period of weeks for full conversion back to the ground state S,S-isomer.

We employed pump−repump−probe spectroscopy to reveal the dynamics and excited state behavior of this compound.[37] Excitation at 355 nm initially produces features consistent with a MLCT excited state. Within 150 ps following excitation, the transient spectrum shows only a single product absorption peak
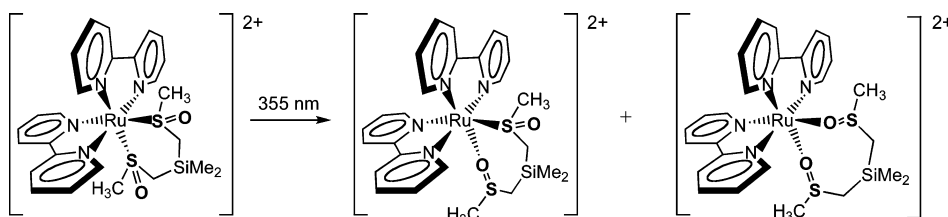
**Figure 5.** Bond line drawings of S,S-, S,O-, and O,O-[Ru(bpy)$_2$(OSSO)]$^{2+}$ and photochemical reactivity displaying both S,O- and O,O-products following single photon excitation of S,S-[Ru(bpy)$_2$(OSSO)]$^{2+}$.

at 400 nm, while the excited state absorptions near 380 nm and in the red region of the spectrum are absent. The lack of MLCT features indicates the formation of a ground state isomer. The product absorption peak at 400 nm is attributed to the S,O-isomer (Figure 4, middle), in accordance with literature precedence.[19,36]

A repump (second pump) beam excites the metastable S,O-isomer producing MLCT excited state features. Within ∼200 ps, a new transient is formed with product absorption peaks at ∼345 and 490 nm. This spectrum is identical to that obtained from bulk photolysis of [Ru(bpy)$_2$(bpSO)]$^{2+}$ and is consistent with a structure in which both sulfoxide ligands are O-bonded (Figure 4, right). In aggregate, the bulk photolysis and time-resolved data provide a picture where irradiation of the ground state S,S-isomer produces an excited state that relaxes to a ground state S,O-isomer. This S,O-isomer is subsequently irradiated to produce a separate excited state that yields the O,O-isomer. Isomerization of the two sulfoxide ligands in [Ru(bpy)$_2$(bpSO)]$^{2+}$ occurs sequentially.

## One Photon Prompts Two Isomerizations

Shown in Figure 5 (left) is the bond line drawing of [Ru(bpy)$_2$(OSSO)]$^{2+}$, where OSSO is dimethylbis-(methylsulfinylmethyl)silane.[34,38] The inner coordination sphere of this complex is identical to that of [Ru-(bpy)$_2$(bpSO)]$^{2+}$, and both adopt C$_2$ symmetry (as deduced from $^1$H NMR spectra and X-ray data) such that the sulfoxide ligands are equivalent. The only structural differences between these complexes are the bridge between the sulfoxides (three atom bridge for OSSO and ethyl bridge for bpSO) and the R group on the sulfoxide (methyl for OSSO and phenyl for bpSO). Thus, one would expect both of these complexes to exhibit similar photochemistry and one would predict the OSSO complex to undergo sequential phototriggered isomerization of the sulfoxide ligands. Much of the reactivity is the same, since both sulfoxides isomerize upon irradiation and the O,O-isomer product thermally reverts to the S,S-isomer. However, bulk photolysis and time-resolved data strongly support the notion that both sulfoxides isomerize following single photon absorption.

In contrast to [Ru(bpy)$_2$(bpSO)]$^{2+}$, bulk photolysis of [Ru(bpy)$_2$(OSSO)]$^{2+}$ with 400 nm light yields only a single isosbestic point invariant throughout the exposure time.[38] The photostationary state reveals absorption maxima at ∼345 and 490 nm, again consistent with a structure with two O atom donors (sulfoxides). Notably absent are isosbestic points indicative of a sequential reaction or features that can be attributed to an S,O-bonded complex (absorption maximum at 400 nm). The time-resolved data are consistent with the bulk photolysis data. Excitation at 400 nm produces transients indicative of a MLCT excited state. This spectrum evolves over time (t = 220 ps) to yield a ground state product spectrum

consistent with the presence of both S,O- and O,O-bonded isomers. Importantly, a single isosbestic point is observed in the evolution of the time-resolved spectra. There is no evidence to indicate that the O,O-bonded isomer is formed after the S,O-isomer. Moreover, power dependence studies do not suggest multiple photon absorption events are operative. Strikingly, these data indicate that both ground state isomers are created simultaneously.

Such results inspire the question of which orbital interactions permit two isomerizations from a single photon absorption event? Shown in Figure 6 are the σ and σ* bonding
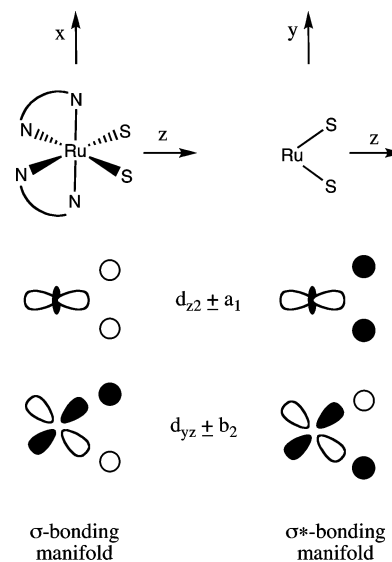


**Figure 6.** Sketch of orbital interactions depicting the S−Ru−S σ- and σ*-bonding manifold. Reproduced with permission from ref 38. Copyright 2014 American Chemical Society.

interactions. The ground state molecule exhibits C$_2$ symmetry when the z-axis is defined so as to bisect the S−Ru−S angle. In this coordinate system and point group, the d$_{z^2}$ orbital has a$_1$ symmetry, and the d$_{yz}$ orbital has b$_2$ symmetry. In conjunction with the a$_1$ and b$_2$ SALCs (symmetry adapted linear combinations) formed from σ lone pairs on the sulfoxide ligands, these Ru orbitals form the σ and σ* basis set. A similar picture can be drawn for the bis O-bonded isomer. With regard to excited state dynamics and isomerization, if the LF states are accessed or populated during excited state evolution, then both sulfoxide ligands are affected. Because we assert that the lowest energy excited state potential energy surface has mixed MLCT/LF character, then isomerization would be facilitated by the presence of the LF states.

The isomerization pathway for these two complexes is similar. Excitation produces a delocalized $^1$MLCT excited state. Solvent preferentially stabilizes one of the bipyridine ligands
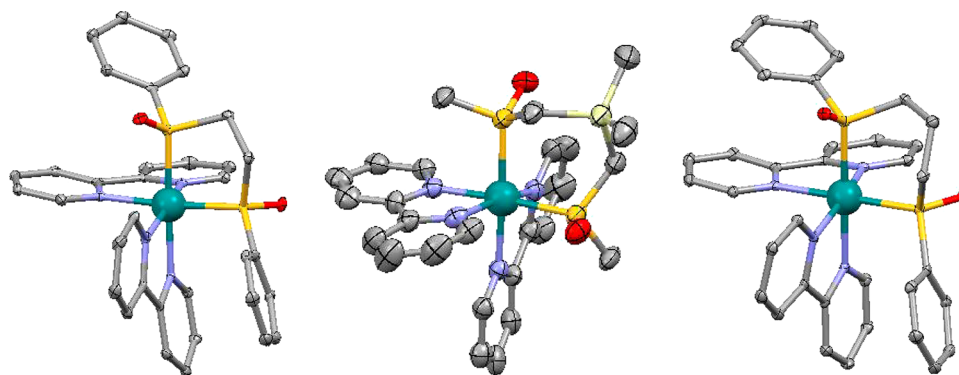
**Figure 7.** Molecular structures of [Ru(bpy)₂(bpSO)]²⁺ (left), [Ru(bpy)₂(OSSO)]²⁺ (center), and [Ru(bpy)₂(bpSOp)]²⁺ (right). Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at 30% probability; Ru is rendered as a ball. Structure of [Ru(bpy)₂(bpSO)]²⁺ reproduced with permission from ref 37. Copyright 2013 American Chemical Society. Structure of [Ru(bpy)₂(OSSO)]²⁺ reproduced with permission from ref 34. Copyright 2008 John Wiley and Sons. Reproduced ([Ru(bpy)₂(bpSOp)]²⁺) with permission from ref 39. Copyright 2014 Royal Society of Chemistry.

resulting in localization of the excited electron, rendering the sulfoxide ligands inequivalent. Concomitant with this process is the formation of the ³MLCT electronic state. These processes occur on a subpicosecond time scale. The electronic changes prompt structural changes that represent the first steps of isomerization. We assume that there are subtle, yet important, differences in these initial events that distinguish the photochemistry of these two complexes.

What are the critical differences between [Ru(bpy)₂(bpSO)]²⁺ and [Ru(bpy)₂(OSSO)]²⁺ that lead to these dramatic photochemical changes in reactivity? Shown in Figure 7 (left, middle) are the molecular structures of these two complexes, as determined by single crystal X-ray diffractometry. Critical metrical data are displayed in Table 1. While both

**Table 1. Bond Distances (Å), S−Ru−S Angles (deg) and Absorption Maxima (nm) for [Ru(bpy)₂(L)]²⁺ Complexes**

| complex | Ru−S | S−Ru−S | $\lambda_{max}$ |
|---|---|---|---|
| [Ru(bpy)₂(bpSO)]²⁺ | 2.248(2)/2.258(2) | 85.9 | 340 |
| [Ru(bpy)₂(bpSOp)]²⁺ | 2.280(1) | 88.8 | 345 |
| [Ru(bpy)₂(OSSO)]²⁺ | 2.293(1) | 92.9 | 348 |

complexes exhibit ground state $C_2$ symmetry (inner coordination sphere is $C_{2v}$), there is a difference in the number of atoms in the chelate ring. The bpSO complex contains five atoms and the OSSO complex contains six atoms. There are also differences in the Ru−S bond distances and chelate bite angles. For [Ru(bpy)₂(bpSO)]²⁺, the Ru−S bond distances are 2.248(2) and 2.258(2) Å; these distances are 2.293(1) Å for [Ru(bpy)₂(OSSO)]²⁺. The distances in [Ru(bpy)₂(bpSO)]²⁺ are shorter than those in [Ru(bpy)₂(OSSO)]²⁺ due to the influence of the phenyl rings on the basicity of the sulfur atoms. Evidence of this electronic influence is also observed in the UV−visible spectra since the MLCT absorption maximum in the bpSO complex is blue (∼340 nm) relative to the OSSO complex (348 nm). Naturally, the S−Ru−S angle in [Ru(bpy)₂(OSSO)]²⁺ is greater (92.92°) than in [Ru(bpy)₂(bpSO)]²⁺ (85.91°). These differences in molecular and electronic structure must suggest the differences in excited state reactivity between these complexes.

We questioned whether the presence of the dimethylsilane group aided rotation of the chelate bridge during isomerization, since it is an obvious difference between these two structures.

Thus, we prepared a complex with a new bis-sulfoxide ligand containing remnant features of both bpSO and OSSO.[39] We created [Ru(bpy)₂(bpSOp)]²⁺, which retained the phenyl groups on each sulfoxide like bpSO but introduced an n-propyl bridge between the sulfoxide functional groups. This is depicted in Figure 7 (right). We predicted that this complex would have structural characteristics between those of both parent complexes. Table 1 displays critical metrical data for all three complexes. For [Ru(bpy)₂(bpSOp)]²⁺, the Ru−S bond distance and S−Ru−S bond angle are 2.280(1) Å and 88.84°, respectively. This bond distance and angle are between those observed for the other two complexes. The MLCT absorption maximum is observed at 345 nm, between those of the other two complexes. These data indicate that the bpSOp ligand has structural characteristics between those of bpSO and OSSO.

The propyl ring analogue displays photochemical (and kinetic) behavior different from either bpSO or OSSO complexes. Time resolved pump−probe spectra of [Ru(bpy)₂(bpSOp)]²⁺ shows the presence of both S,O- and O,O-bonded isomers indicating a similar reactivity to [Ru(bpy)₂(OSSO)]²⁺, although the O,O-isomer is produced in lower yield (S,O-/O,O-isomer is 1:0.08). This is in contrast to the OSSO complex where with 400 nm excitation, the S,O-/O,O-isomer ratio is ∼1. This result also appears to indicate the importance of rotation within the chelate ring for isomerization. Indeed, methylsilane exhibits a smaller rotational barrier (1.7 kcal mol⁻¹) than ethane (2.9 kcal mol⁻¹) due to the longer C−Si bond, which reduces repulsive internuclear interations in the eclipsed conformation. These studies show that modifications of the chelate ring can alter excited state isomerization reactivity.

## ■ SULFOXIDE ISOMERIZATION ON OSMIUM

We observe phototriggered S → O isomerization in [Os(bpy)₂(dmso)₂]²⁺ and [Os(bpy)₂(pySOCF₃)]²⁺, where py-SOCF₃ is 2-((trifluoroethylsulfinyl)methyl)pyridine.[33,40] Since the LF states are approximately 30% higher in energy in Os²⁺ versus Ru²⁺, this suggests that the LF states are not *required* for isomerization but rather isomerization is *facilitated* by their presence. Interestingly, the related compound [Os(bpy)₂(pySO)]²⁺, where pySO is 2-((isopropylsulfinyl)methyl)pyridine, does not feature phototriggered isomerization of the sulfoxide. One explanation for this difference is that the Os−S bond is weaker in the complex with a fluorinated group

$(-CH_2CF_3)$ on the sulfoxide in comparison to the complex with a hydrocarbon group $(-CH(CH_3)_2)$ on the sulfoxide. Spectroscopic (UV−visible, NMR, and IR) and electrochemical data are consistent with this interpretation. We note that phototriggered isomerization is not observed in [Os-(bpy)$_2$(pyESO)]$^{2+}$, where pyESO is 2-((isopropylsulfinyl)-ethyl)pyridine but that S → O and O → S isomerization is observed following oxidation of Os$^{2+}$ and reduction of Os$^{3+}$, respectively.[41] We speculate that the longer Os−S bonds and larger bite angle associated with an expanded chelate must weaken the Os−S bond enough to permit isomerization following electrochemical oxidation. This suggestion is in accord with our observations regarding the reactivity of [Ru(bpy)$_2$(OSSO)]$^{2+}$, where one photon absorption prompts two isomerizations. In comparison to the complex with the fluorinated sulfoxide above, the data suggest that the extent of charge transfer in the excited state for [Os(bpy)$_2$(pyESO)]$^{2+}$ does not produce an oxidized osmium capable of prompting isomerization. This interpretation is consistent with results obtained earlier on ruthenium terpyridine sulfoxide complexes where we observed that isomerization could be tuned in the presence of $\pi$-basic ancillary ligands.[27,42−44] It seems that by balancing the ground state Os−S bond strength through modulation of the Lewis basicity of the S atom and the chelate ring size, one should be able to design efficient photochromic osmium sulfoxide compounds.

## FUTURE CONSIDERATIONS

An important caveat with time-resolved pump−probe measurements is that they only report on changes involving the electronic transitions of reactant and products. The technique is blind to structural or conformational changes associated with the sulfoxide ligand(s). Our assertions regarding the nature of these structural changes are largely speculative. The application of structurally sensitive techniques (e.g., time-resolved X-ray absorption spectroscopy, femtosecond stimulated Raman scattering, or resonance Raman) to these compounds would greatly enhance our understanding of their reactivity. However, it is certain that as the Ru−S bonds increase in distance, one expects MLCT states to rise in energy and LF states to decrease in energy. The technique is similarly blind to changes in the oxidation state of the ruthenium. Our proposal of an excited state potential energy surface that is a mixture of LF and MLCT character is based on our spectroscopic observations and accommodates computational results showing that the MC states are lowest in energy. Moreover, the observation of isomerization on Os$^{2+}$ precludes a model in which the excited state leading to isomerization is entirely LF in character. As there is no single technique that will provide all of this information, we will continue to improve our understanding of these complexes by relying upon results from many experimental investigations including computations.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: rackj@ohio.edu.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

### Biographies

**Albert W. King** earned his B.S. degree (2010) from Walsh University. He is a graduate student at Ohio University.

**Lei Wang** earned his B.S. degree (2010) from Hebei University of Technology (China). He is a graduate student at Ohio University.

**Jeffrey J. Rack** obtained his B.S. (1991) degree from Clemson University and Ph.D (1996) degree from Colorado State University. He held postdoctoral appointments at Caltech and the Los Alamos National Laboratory prior to starting at Ohio University in 2001.

## ■ REFERENCES

(1) *Molecular Machines*; Kelly, T. R., Ed.; Springer-Verlag: Berlin, Germany, 2005; Vol. 262.

(2) *Molecular Switches*, 2nd ed.; Feringa, B. L., Browne, W. R., Eds.; Wiley-VCH: Weinheim, Germany, 2011.

(3) *Photochromism Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, The Netherlands, 2003.

(4) Rack, J. J. Electron Transfer Triggered Sulfoxide Isomerization in Ruthenium and Osmium Complexes. *Coord. Chem. Rev.* **2009**, *253*, 78−85.

(5) Yeh, A.; Scott, N.; Taube, H. S to O and O to S Linkage Isomerization in Sulfoxide Complexes of Pentaammineruthenium. *Inorg. Chem.* **1982**, *21*, 2542−2545.

(6) Benet-Buchholz, J.; Comba, P.; Llobet, A.; Roeser, S.; Vadivelu, P.; Wiesner, S. The RuIV═O Catalyzed Sulfoxidation: A Gated Mechanism Where O to S Linkage Isomerization Switches between Different Efficiencies. *Dalton Trans.* **2010**, *39*, 3315−3320.

(7) Gong, L.; Lin, Z.; Harms, K.; Meggers, E. Isomerization-Induced Asymmetric Coordination Chemistry: From Auxiliary Control to Asymmetric Catalysis. *Angew. Chem., Int. Ed.* **2010**, *49*, 7955−7957.

(8) Li, Z.-Z.; Yao, S.-Y.; Wu, J.-J.; Ye, B.-H. In Situ Generation of Sulfoxides with Predetermined Chirality via a Structural Template with a Chiral-at-Metal Ruthenium Complex. *Chem. Commun.* **2014**, *50*, 5644−5647.

(9) Suzuki, S.; Sakamoto, R.; Nishihara, H. Two-Way Linkage Photoisomerization of [Ru(2,2′:6′,2″-terpyridine)(6-{methylsulfinyl}-methyl}picolinate)]BF$_4$. *Chem. Lett.* **2013**, *42*, 17−18.

(10) To quote George Box, "Essentially, all models are wrong, but some are useful." Box, G. E. P.; Draper, N. R. *Empirical Model Building and Response Surfaces*; John Wiley and Sons: New York, 1987; p 424.

(11) Albani, B. A.; Durr, C. B.; Turro, C. Selective Photoinduced Ligand Exchange in a New Tris-Heteroleptic Ru(II) Complex. *J. Phys. Chem. A* **2013**, *117*, 13885−13892.

(12) Durham, B. D.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. Photochemistry of [Ru(bpy)$_3$]$^{2+}$. *J. Am. Chem. Soc.* **1982**, *104*, 4803−4810.

(13) Malouf, G.; Ford, P. C. Photochemical Reaction Pathways fo Ruthenium(II) Complexes. Evidence Regarding the Reactive Excited State(s) from Metal-to-Ligand Charge Transfer Excitation of Ru-(NH$_3$)$_5$py$^{2+}$ and Related Complexes. *J. Am. Chem. Soc.* **1970**, *96*, 601−603.

(14) Garner, R. N.; Joyce, L. E.; Turro, C. Effect of Electronic Structure on the Photoinduced Ligand Exchange of Ru(II) Polypyridine Complexes. *Inorg. Chem.* **2011**, *50*, 4384−4391.

(15) Liu, Y.; Turner, D. B.; Singh, T. N.; Angeles-Boza, A. M.; Chouai, A.; Dunbar, K. R.; Turro, C. Ultrafast Ligand Exchange: Detection of a Pentacoordinate Ru(II) Intermediate and Product Formation. *J. Am. Chem. Soc.* **2009**, *131*, 26−27.

(16) Fredin, L. A.; Pápai, M.; Rozsályi, E.; Vankó, G.; Wärnmark, K.; Sundström, V.; Persson, P. Exceptional Excited-State Lifetime of an Iron(II)-N-Heterocyclic Carbene Complex Explained. *J. Phys. Chem. Lett.* **2014**, *5*, 2066−2071.

(17) Österman, T.; Abrahamsson, M.; Becker, H.-C.; Hammarström, L.; Persson, P. Influence of Triplet State Multidimensionality on Excited State Lifetimes of Bis-tridentate Ru(II) Complexes: A Computational Study. *J. Phys. Chem. A* **2012**, *116*, 1041−1050.

(18) Howerton, B. S.; Heidary, D. K.; Glazer, E. C. Strained Ruthenium Complexes Are Potent Light-Activated Anticancer Agents. *J. Am. Chem. Soc.* **2012**, *134*, 8324−8327.

(19) Smith, M. K.; Gibson, J. A.; Young, C. G.; Broomhead, J. A.; Junk, P. C.; Keene, F. R. Photoinduced Ligand Isomerization in Dimethylsulfoxide Complexes of Ruthenium(II). *Eur. J. Inorg. Chem.* **2000**, 1365−1370.

(20) Calvert, J. M.; Meyer, T. J. Polypyridine Complexes of Ruthenium(II) Bound to Poly(4-vinylpyridine). Synthesis, Characterization, and Thin-Film Electrochemistry of a Series of Bis(bipyridine) Metallopolymers. *Inorg. Chem.* **1982**, *21*, 3978−3989.

(21) Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. Oxygen Atom Transfer in the Oxidations of Dimethyl Sulfide and Dimethylsulfoxide by $[(bpy)_2(py)Ru(O)]^{2+}$. *Inorg. Chem.* **1987**, *26*, 779−781.

(22) Coe, B. J.; Meyer, T. J.; White, P. S. Control of Axial Ligand Substitution in *trans*-Bis(2,2′-bipyridine)(ruthenium(II) Complexes. Crystal and Molecular Structure of *trans*-(4-Ethylpyridine)-(dimethylsulfoxide)-bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate, *trans*-$[Ru(bpy)_2(4\text{-Etpy})(DMSO)](PF_6)_2$. *Inorg. Chem.* **1993**, *32*, 4012−4020.

(23) Calligaris, M. Structure and Bonding in Metal Sulfoxide Complexes: An Update. *Coord. Chem. Rev.* **2004**, *248*, 351−375.

(24) Göttle, A. J.; Alary, F.; Dixon, I. M.; Heully, J. L.; Boggio-Pasqua, M. Unravelling the S → O Linkage Photoisomerization Mechanisms in *cis*- and *trans*-$[Ru(bpy)_2(dmso)_2]^{2+}$ Using Density Functional Theory. *Inorg. Chem.* **2014**, *53*, 6752−6760.

(25) Göttle, A. J.; Dixon, I. M.; Alary, F.; Heully, J. L.; Boggio-Pasqua, M. Adiabatic versus Nonadiabatic Photoisomerization in Photochromic Ruthenium Sulfoxide Complexes: A Mechanistic Picture from Density Functional Theory Calculations. *J. Am. Chem. Soc.* **2011**, *133*, 9172−9174.

(26) McClure, B. A.; Mockus, N. V.; Butcher, D. P.; Lutterman, D. A.; Turro, C.; Petersen, J. L.; Rack, J. J. Photochromic Ruthenium Sulfoxide Complexes: Evidence for Isomerization through a Conical Intersection. *Inorg. Chem.* **2009**, *48*, 8084−8091.

(27) Lutterman, D. A.; Rachford, A. A.; Rack, J. J.; Turro, C. Electronic and Steric Effects on the Photoisomerization of Dimethylsulfoxide Complexes of Ru(II) Containing Picolinate. *J. Phys. Chem. Lett.* **2010**, *1*, 3371−3375.

(28) McClure, B. A.; Abrams, E. R.; Rack, J. J. Excited State Distortion in Photochromic Ruthenium Sulfoxide Complexes. *J. Am. Chem. Soc.* **2010**, *132*, 5428−5436.

(29) Braterman, P. S.; Song, J.-I.; Peacock, R. D. Electronic Absorption Spectra of the Iron(II) Complexes of 2,2′-Bipyridine, 2,2′-Bipyrimidine, 1,10-Phenanthroline, and 2,2′:6′,2″-Terpyridine and Their Reduction Products. *Inorg. Chem.* **1992**, *31*, 555−559.

(30) Damrauer, N. H.; McCusker, J. K. Ultrafast Dynamics in the Metal-to-Ligand Charge Transfer Excited-State Evolution of $[Ru(4,4′\text{-}diphenyl\text{-}2,2′\text{-bipyridine})_3]^{2+}$. *J. Phys. Chem. A* **1999**, *103*, 8440−8446.

(31) Sun, Q.; Mosquera-Vazquez, S.; Daku, L. M. L.; Guénée, L.; Goodwin, H. A.; Vauthey, E.; Hauser, A. Experimental Evidence of Ultrafast Quenching of the $^3$MLCT Luminescence in Ruthenium(II) Tris-bipyridyl Complexes via a $^3$dd State. *J. Am. Chem. Soc.* **2013**, *135*, 13660−13663.

(32) Li, H.; Zhang, L.; Lin, H.; Fan, X. A DFT-D Study on the Electronic and Photophysical Properties of Ruthenium(II) Complex with a Chelating Sulfoxide Group. *Chem. Phys. Lett.* **2014**, *604*, 10−14.

(33) Mockus, N. V.; Petersen, J. L.; Rack, J. J. Subnanosecond Isomerization in an Osmium-Dimethylsulfoxide Complex. *Inorg. Chem.* **2006**, *45*, 8−10.

(34) Mockus, N. V.; Rabinovich, D.; Petersen, J. L.; Rack, J. J. Femtosecond Isomerization in a Photochromic Molecular Switch. *Angew. Chem., Int. Ed.* **2008**, *47*, 1458−1461.

(35) Rachford, A. A.; Petersen, J. L.; Rack, J. J. Phototriggered Sulfoxide Isomerization in $[Ru(pic)_2(dmso)_2]$. *Dalton Trans.* **2007**, 3245−3251.

(36) Rack, J. J.; Mockus, N. V. Room-Temperature Photochromism in *cis*- and *trans*-$[Ru(bpy)_2(dmso)_2]^{2+}$. *Inorg. Chem.* **2003**, *42*, 5792−5794.

(37) King, A. W.; Jin, Y.; Engle, J. T.; Ziegler, C. J.; Rack, J. J. Sequential Picosecond Isomerizations in a Photochromic Ruthenium Sulfoxide Complex Triggered by 2-Color Pump-Repump-Probe Spectroscopy. *Inorg. Chem.* **2013**, *52*, 2086−2093.

(38) Garg, K.; King, A. W.; Rack, J. J. One Photon Yields Two Isomerizations: Large Atomic Displacements during Electronic Excited State Dynamics in Ruthenium Sulfoxide Complexes. *J. Am. Chem. Soc.* **2014**, *136*, 1856−1863.

(39) King, A. W.; Malizia, J. P.; Engle, J. T.; Ziegler, C. J.; Rack, J. J. Ultrafast Spectroscopy and Structural Characterization of a Photochromic Isomerizing Ruthenium bis-Sulfoxide Complex. *Dalton Trans.* **2014**, *43*, 17847−17855.

(40) Garg, K.; Paris, S. I. M.; Rack, J. J. A Flexible Chelate Leads to Phototriggered Isomerization in a Photochromic Osmium Sulfoxide Complex. *Eur. J. Inorg. Chem.* **2013**, *7*, 1142−1148.

(41) Garg, K.; Engle, J. T.; Ziegler, C. J.; Rack, J. J. Ground and Excited State Isomerization Dynamics in Analogous Ruthenium and Osmium Sulfoxide Complexes. *Chem.—Eur. J.* **2013**, *19*, 11686−11695.

(42) Lutterman, D. A.; Rachford, A. A.; Rack, J. J.; Turro, C. Theoretical Insight on the S→O Bound Photoisomerization of DMSO Complexes of Ru(II). *J. Phys. Chem. A* **2009**, *113*, 11002−11006.

(43) Rachford, A. A.; Petersen, J. L.; Rack, J. J. Designing Molecular Bistability in Ruthenium Dimethylsulfoxide Complexes. *Inorg. Chem.* **2005**, *44*, 8065−8075.

(44) Rack, J. J.; Rachford, A. A.; Shelker, A. M. Turning Off Phototriggered Linkage Isomerizations in Ruthenium Dimethyl Sulfoxide Complexes. *Inorg. Chem.* **2003**, *42*, 7357−7359.