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Perspective

A Future Perspective on Phototriggered Isomerizations of Transition Metal Sulfoxides and Related Complexes

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ABSTRACT: Photochromic molecules are examples of light-activated bistable molecules. We highlight the design criteria for a class of ruthenium and osmium sulfoxide complexes that undergo phototriggered isomerization of the bound sulfoxide. The mode of action in these complexes is an excited-state isomerization of the sulfoxide from S-bonded to O-bonded. We discuss the basic mechanism for this transformation and highlight specific examples that demonstrate the effectiveness and efficiency of the isomerization. We subsequently discuss future research directions within the field of phototriggered sulfoxide isomerizations on transition metal polypyridine complexes. These efforts involve new synthetic directions, including the choice of metal as well as new ambidentate ligands for isomerization.

■ INTRODUCTION

Photochromism[1,2] is situated at the nexus of photochemistry and molecular machines. This field of study encompasses the traditional disciplines of organic, inorganic, and physical chemistry. These compounds transduce photonic energy to potential energy efficiently and rapidly to produce a new metastable isomer on the ground-state potential energy surface. Accordingly, their excited-state potential energy surfaces are complex and involve strong electronic−nuclear coupling and surface mixing not featured in most other molecules. The study of bistable molecules thus provides a convenient architecture to study surface crossing and energy transduction processes.

Bistability is a fundamental property that is found throughout biology, engineering, computing, materials science, and chemistry. Bistability is manifested in a variety of feedback loops in biological systems and is seen in classical mechanics in the form of rotors and ratchets. Mathematically, in one dimension the term describes a simple system with two low-lying states separated by a single unstable higher-lying position connecting the two. The simplest analytical form that describes this relationship is $f(x) = x^4 - x$.[2] This equation corresponds to a chemical reaction in which $\Delta G^\circ_{\mathrm{rxn}} = 0$, such that both stable forms or isomers of the bistable molecule exhibit the same free energy, separated by a single transition state. The inclusion of an x^3 term results in a curve in which one of the stable states is lower in energy than the other, thus corresponding to a chemical reaction where $\Delta G^\circ_{\mathrm{rxn}} \neq 0$. In chemical terms, the higher lying minimum is often referred to as metastable, since it is necessarily unstable relative to the lowest energy minimum. A particle or molecule temporarily found in the higher lying minimum will revert to the lowest energy minimum at some temperature after some amount of time. It is important to note that bistability only requires two local minima. It makes no requirement on the height of the barrier separating the two minima, and thus there is no stipulation on the lifetime of the metastable state as a qualification for bistability.

Group 6 (Fe, Ru, and Os) polypyridine complexes, their many derivatives, and neighboring metals (Cr, Mo, W, Re, Rh, and Ir) are utilized in a wide variety of photochemical schemes.[3] The attraction is due to multiple oxidation states that are stable relative to ligand substitution and that are well matched with many ligand reduction (and oxidation) potentials. While the vast majority of photochromic compounds are metal-free,[4,5] we sought to create a class of photochromic complexes comprising transition metal complexes that exploit the concepts and synthetic strategies that are well-developed for group 6 polypyridine complexes.

■ DESIGN CRITERIA

The creation of *any* photoactive chromophore requires the definition and optimization of specific design principles. Many present efforts in the design of transition metal chromophores with specific thermodynamic and kinetic parameters find inspiration in the so-called "Flash-Quench" scheme reported by Chang, Winkler, and Gray.[6] By relying on an essentially colorless quencher ($[\mathrm{Ru(NH_3)_6}]^{3+}$) at sufficient concentrations, they found that visible excitation of a covalently attached $[\mathrm{Ru(bpy)_3}]^{2+}$-type chromophore (bpy is 2,2′-bipyridine) could effectively generate a high-potential *ground-state* oxidant in large yield for intramolecular protein electron transfer (ET). This procedure balances kinetics and thermodynamics for long-range ET and obviates the difficulties associated with

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distance and excited-state lifetime in photoinduced ET. Dye-sensitized solar cells embrace many of these kinetic and thermodynamic design parameters in the conversion of light to electricity.[7,8] Similarly, the recent activity to create iron and other first-row transition metal chromophores sought to stabilize metal-to-ligand charge-transfer (MLCT) states relative to ligand field (LF) states.[9−13] Moreover, effective photocatalytic redox mediators must feature reducing equivalents formed by light at negative enough potentials to reduce a variety of organic substrates.[14] Of course, all of these efforts were based on the thousands of previous reports involving a wide range of dyes and quenchers for the study of electron and energy transfer.

The creation of bistable photochromic complexes is no different. Our ruthenium and osmium sulfoxide photochemistry conjoins the electrochemistry of $[Ru(NH_3)_5(dmso)]^{2+}$ (dmso is dimethyl sulfoxide) and the photophysics of $[Ru(bpy)_3]^{2+}$. Reported by Taube in 1982, the cyclic voltammogram of $[Ru(NH_3)_5(dmso)]^{2+}$ is best described by an *ECEC* mechanism, where S→O isomerization follows electrochemical oxidation of Ru^{2+} to produce Ru^{3+}.[15] On the reverse scan, electrochemical reduction of Ru^{3+} to produce Ru^{2+} prompts O→S isomerization. The appearance of the voltammogram reflects the scan rate, switching potential, and rates of isomerization. As explained by Taube and later researchers, the thermodynamic driving force for this reaction are the preferences of the O-bonded sulfoxide for the Ru^{3+} ion and of the S-bonded sulfoxide for the Ru^{2+} ion.[16−20]

The photophysics of ruthenium polypyridine complexes is well known.[21] Visible excitation of $[Ru(bpy)_3]^{2+}$ creates a thermally equilibrated excited state in a few hundred femtoseconds that persists long enough for bimolecular reactivity (~1 μs).[22] This MLCT excited state is best described as a Ru^{3+} central ion and a reduced bipyridine. For the design of photochromes based on $[Ru(NH_3)_5(dmso)]^{2+}$ and $[Ru(bpy)_3]^{2+}$, we simply questioned whether S→O isomerization could be phototriggered in a heteroleptic ruthenium complex containing a polypyridine (bipyridine) ligand and a sulfoxide ligand. We posited that the Ru^{3+} ion formed from visible excitation in the MLCT excited state would prompt isomerization of the sulfoxide, yielding an O-bonded metastable state.[23,24]

Thus, the creation of photochromic transition metal complexes requires an ambidentate ligand (e.g., sulfoxide), a metal atom or ion that is stable to ligand substitution in two successive oxidations states (e.g., Ru^{2+}, Ru^{3+}), and a ligand with low-lying π* orbitals for MLCT excitation (e.g., bipyridine). The other coordination sites are then available for fine-tuning the reactivity or spectroelectrochemical characteristics of the specific coordination complex (Figure 1). Based on these concepts, we have created a large family of photochromic ruthenium and osmium polypyridine sulfoxide complexes. The sulfoxide provides the mode of action for these photochromic complexes and is featured within a chelate. The R′ group has been shown to modulate the quantum yield of isomerization and the absorption maximum. The choice of X (e.g., pyridine, sulfoxide, benzoate) determines the quantum yield of isomerization and the number of sulfoxide units bonded to Ru. The number of atoms in the chelate linker provides flexibility, which affects the quantum yield of isomerization and intramolecular vibrational energy redistribution pathways. We have also discovered that the identity of the central metal ion affects ground-state bond strengths and excited-state behavior (e.g., Os^{2+} vs Ru^{2+}). In the next sections, these details will be discussed, which will then be followed by a discussion of future research directions.

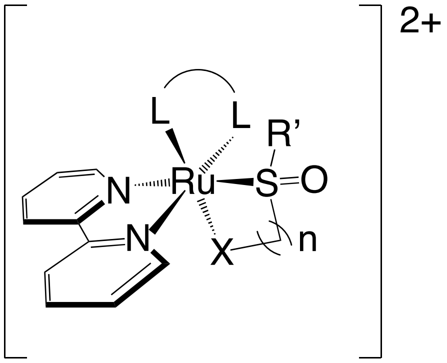


Figure 1. Generic chemical sketch of ruthenium polypyridine sulfoxide structure.

PHOTOCHROMIC RUTHENIUM PHOSPHINE SULFOXIDE COMPLEXES

The ultimate goal of photochemistry has been to use light to selectively and specifically break and make bonds either within a single molecule or between molecules. Photochromic compounds and complexes naturally convert photonic energy to potential energy for these purposes. However, it is widely recognized by those in this field that seemingly small changes in structure can have rather dramatic changes in photochemistry. Indeed, we experienced this in our study of $[Ru^{II}(tpy)(L)(dmso)]^{n+}$ (tpy is 2,2′:6′,2″-terpyridine; dmso is dimethyl sulfoxide; L is a variably replaced ligand that may be charged or neutral) photochromes, where the presence of strong π-donating O-donor ligands (e.g., acac, oxalate, malonate) prevented isomerization from occurring.[25,26] In those cases, we surmised that the π-donor ligands modified the MLCT nature of the electronic transition to contain more ligand-to-ligand character, thus reducing the contribution from metal oxidation. Since isomerization is prompted by oxidation in this model, transition metal complexes that do not feature metal oxidation will not prompt isomerization. We wanted to revisit this concept of structural changes to elicit control of photoisomerization in chelating sulfoxides, but our study of benzoate and pyridine sulfoxides revealed only modest control.[27] We felt a new chelating sulfoxide architecture based on phosphines would be successful, as phosphines are widely employed in organometallic chemistry to modulate electron density at the metal.[28] This is achieved by variation of the R groups on the phosphine, permitting phosphines to be σ-only donors (e.g., PR_3, R is alkyl), σ- and π-donors (e.g., phosphites), or σ- and π-acceptors (e.g., PPh_3, Ph is phenyl).[28] Furthermore, the separate works of Darensbourg,[29,30] Grapperhaus,[31−33] and Igau[34−38] all suggest this to be a promising approach. Specifically, Igau and co-workers reported the effect of structural changes of phosphine bonding on the spectral and electrochemical properties of $[Ru(tpy)(bpy)(PR_3)]^{2+}$. For example, the $Ru^{3+/2+}$ reduction potential may vary by nearly 300 mV, when R varies from -OPh ($E°′$ = 1.61 V vs SCE) to -^{i}Pr (^{i}Pr; $E°′$ = 1.35 V vs SCE), with similar changes in the observed absorption maxima (-OPh: 401 nm; -^{i}Pr: 461 nm).[34]

While phosphine−sulfur chelating ligands are not uncommon,[39] phosphine−sulfoxide ligands are rare. Many easily accessible phosphine−sulfur chelates contain a thiolate, where alkylation does not readily yield the thioether exclusively. Recently, there has been an interest in the creation of chiral phosphine sulfoxides (SOP), which have shown great effectiveness in asymmetric allylic alkylation and asymmetric hydrofluorination.[40,41] In addition, photochemical schemes have been developed that allow for the isolation of chiral sulfoxides,[42−44] and in some cases a chiral sulfoxide has been employed to create chiral ruthenium complexes.[45,46]

We chose to focus on a triphenylphosphine unit that could be structurally modified on the phosphine unit and contain a conserved methylsulfinyl group for isomerization.[47] We structurally characterized three of these complexes (Figure 2), in which the atom or group at the *para*-position of the phenyl ring (relative to P) was H, OCH_3, or CF_3. We designated these complexes $[Ru(bpy)_2(L1O_H)]^{2+}$, $[Ru(bpy)_2(L2O_{OCH_3})]^{2+}$, and $[Ru(bpy)_2(L3O_{CF_3})]^{2+}$.

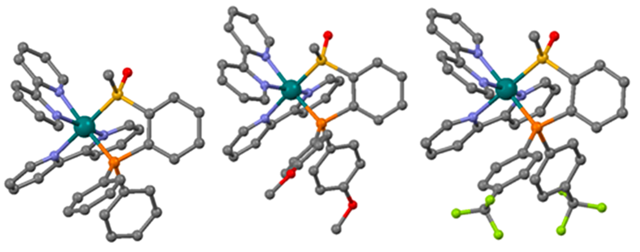


Figure 2. Molecular structures of $RuL1O_H$ (left), $RuL2O_{OCH_3}$ (center), and $RuL3O_{CF_3}$ (right). Reprinted with permission from ref 47. Copyright 2018 American Chemical Society.

Shown in Figure 3A are the UV−visible absorption spectra for these three complexes. One immediately notices that, while the spectra have similar shape and intensity, their absorption maxima are slightly shifted relative to one another. This indicates that the *para*-substituent (H, OCH_3, CF_3), despite being quite far away in position and distance, exerts an electronic influence on the MLCT maximum. Presumably, this is through modulation of the electron density at Ru.[28] Bulk photolysis of $[Ru(bpy)_2(L1O_H)]^{2+}$ or $[Ru(bpy)_2(L3O_{CF_3})]^{2+}$ yields dramatic changes in the UV−visible spectra of these complexes, and representative spectra are displayed in Figure 3B for $[Ru(bpy)_2(L3O_{CF_3})]^{2+}$. Irradiation throughout the MLCT absorption profile results in loss of intensity at the MLCT maximum, with a concomitant and monotonic rise of intensity at longer wavelengths, finally producing a new absorption maximum at 422 nm. Tight isosbestic points are observed at 332 and 376 nm, indicating direct conversion from one isomer to another on this time scale. That these absorption changes are reversible in alcohol, halocarbon, and acetonitrile solvents is strongly indicative of an intramolecular reaction. We assign this new spectrum to the O-bonded isomer, which is corroborated by literature reports. For example, Wolf and coworkers have examined similar species (e.g., $[Ru(bpy)_2(PO)]^{2+}$, where PO is 2-diphenylphosphinoanisole), where the $[Ru(bpy)_2]^{2+}$ coordination sphere contains both a P and O donor.[48−50] The absorption maximum for that species is 412 nm, which compares well to that reported above for $[Ru(bpy)_2(L3O_{CF_3})]^{2+}$. The related absorption maxima for S- and O-$[Ru(bpy)_2(L1O_H)]^{2+}$ are 351 and 436 nm, respectively.

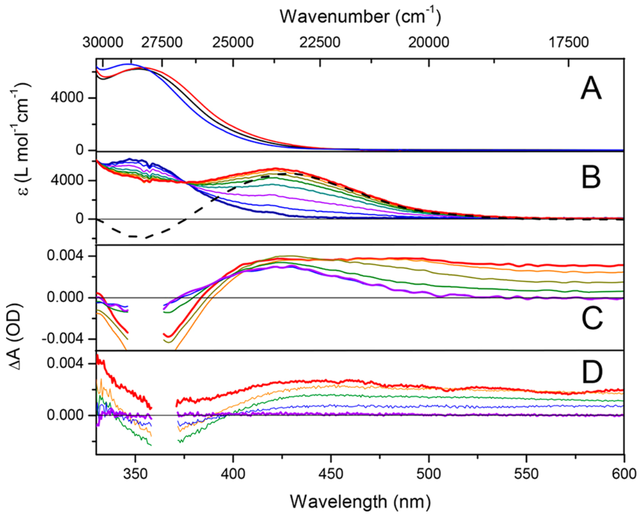


Figure 3. (A) Absorption spectra for S-$[(bpy)_2Ru(L1O_H)]^{2+}$ (black), S-$[(bpy)_2Ru(L2O_{OCH_3})]^{2+}$ (red), and S-$[(bpy)_2Ru(L3O_{CF_3})]^{2+}$ (blue). (B) Spectra obtained from bulk photolysis (λ_{exc} 355 nm) of $[(bpy)_2Ru(L3O_{CF_3})]^{2+}$ in dichloroethane solution. Spectra were obtained at 80 s intervals. Black dashed trace is the difference spectrum (O-isomer − S-isomer) extracted from bulk photolysis data. (C) Time-resolved spectra of $[(bpy)_2Ru(L3O_{CF_3})]^{2+}$ obtained at different pump−probe delays of 2.0 ps (red), 20.1 ps (orange), 202 ps (olive green), 2000 ps (green), and 4990 ps (violet). The new absorption maximum centered at 422 is evidence of a photoproduct, consistent with the bulk photolysis data. (D) Time-resolved spectra of $[(bpy)_2Ru(L2O_{OCH_3})]^{2+}$ obtained at different pump−probe delays of 0.41 ps (red), 2.51 ps (orange), 199 ps (green), 1000 ps (blue), and 4660 ps (violet). These traces provide no evidence for the formation of a photoproduct (isomerization), consistent with the bulk photolysis data. Reprinted with permission from ref 47. Copyright 2018 American Chemical Society.

Femtosecond pump−probe spectroscopy was utilized to reveal the details of the spectral changes observed in the bulk photolysis of the complexes. Shown in Figure 3C are the transient spectra for $[Ru(bpy)_2(L3O_{CF_3})]^{2+}$ collected at different pump−probe time delays. Initial traces show a deep bleach (negative absorbance) feature corresponding to the MLCT absorption (black dashed trace, Figure 3B), indicating that this feature is due to loss of the ground state upon irradiation. These traces also show a broad excited-state absorption (ESA) from ∼380 nm throughout the visible (600 nm) and into the near-IR (not depicted). One does not observe an ESA peak near 380 nm, typical of MLCT states, in part because the MLCT absorption maximum lies very near this wavelength. As time evolves, the long-wavelength ESA decreases in intensity, indicating loss of the unreduced pπ bpy → Ru^{III} dπ LMCT transition. This process signifies formation of a Ru^{II} ground state. During this time, the bleach also loses intensity, ultimately producing a final transient with a shallow bleach at ∼360 nm, a new absorption maximum at ∼425 nm, and no absorbance in the red. The final transient (4990 ps; purple trace, Figure 3C) is strongly reminiscent of the final spectrum obtained from bulk photolysis (red trace, Figure 3B). In conjunction with the quantum yield of isomerization ($\Phi_{S\rightarrow O}$ = 0.8), kinetic analysis reveals a time constant for isomerization of 630 ± 80 ps. For $[Ru(bpy)_2(L1O_H)]^{2+}$, $\Phi_{S\rightarrow O}$ = 0.2, resulting in a time constant for isomerization of 740 ± 60 ps.

In contrast, neither bulk photolysis nor transient absorption spectroscopy reveals any evidence for isomerization for $[Ru(bpy)_2(L2O_{OCH3})]^{2+}$, thus demonstrating $\Phi_{S\rightarrow O} = 0.0$. Indeed, the transient spectra of this complex are displayed in Figure 3D. These spectra are typical of $[Ru(bpy)_3]^{2+}$-type chromophores with MLCT states. Importantly, the final transient 4660 ps is indistinguishable from that of the zero line, supporting the bulk photolysis data (not shown) indicating that a photochemical product is not formed upon irradiation at any wavelength in resonance with the MLCT absorption. Taken together, these data illustrate that phosphine ligands provide extraordinary control of the photochemistry of this family of complexes.

It is remarkable that the small structural change described above has such a dramatic effect on the photochemical properties. We are continuing our study of these complexes and note anecdotally that complexes with electron-donating ligands (e.g., alkyl) do not show evidence of isomerization. Many also show irreversible electrochemistry, which is in contrast to the report by Igau and co-workers on phosphines in $[Ru(tpy)(bpy)PR_3]^{2+}$.[34] These studies suggest that the photochemistry of ruthenium complexes containing traditional organometallic ligands deserves further attention.

CORRELATING ELECTRONIC STRUCTURAL CHANGES WITH ATOMIC STRUCTURAL CHANGES

As stated above, photochromic compounds transduce photonic energy to potential energy for excited-state bond-breaking and bond-making. Thus, while visible transient absorption spectroscopy has revealed photophysical and photochemical mechanisms, these data do not uncover details regarding the structural changes that occur following excitation. An enduring and promising area of study for the future is the collection of time-resolved structural or atom-specific spectroscopic data that is subsequently correlated with electronic spectroscopic data, preferably in the same medium.[51−53] It is expected that kinetic analysis and results will not be identical, as atoms move much more slowly than electrons. Indeed, it is well known that femtosecond TR-IR kinetic data do not always align with visible pump−probe data on this same time scale.[54,55] While there may be many approaches to this goal, there appear to be three strategies that may well generate the most interesting results: TR-XAS, time-resolved photocrystallography, and TR-IR spectroscopy. The objectives of these comparisons are to gain a more thorough understanding of the photochemical mechanism of these complexes and to increase our knowledge of excited-state electronic−nuclear coupling.

While TR-XAS has been employed with great success to elucidate photophysical mechanisms in transition metal complexes,[56,57] we know of few such studies involving photochromic compounds. For example, Chernyshev, Guda and co-workers reported Zn^{2+} release from a Zn^{2+}-coordinated merocyanine (MC) dye complex from Zn K-edge X-ray absorption near-edge structure (XANES) spectroscopy.[58] Irradiation of the Zn^{2+}-MC dye prompts release of Zn^{2+} and subsequent photocyclization to produce the ground-state spiropyran. The reaction was also monitored by UV−visible spectroscopy, as Zn^{2+} coordination greatly enhances the extinction coefficient of the ring-opened (MC) isomer. Importantly, the XANES spectra revealed different coordination environments about Zn^{2+} during photorelease, which was not observed in the visible spectra. This comparison demonstrates the promise of this technique. A challenge for the application of TR-XAS to most organic photochromes is the lack of suitable nuclei to probe, though the well-studied dithienylethenes (which contain two sulfur atoms) should be good candidates.

We recently published an S K-edge and Ru L_3-edge TR-XAS study of $[Ru(bpy)_2(pyeso)]^{2+}$ (pyeso is 2-((isopropylsulfinyl)-ethyl)pyridine) in combination with DFT and TD-DFT methods.[59] A striking result is the relative complexity of the kinetic model required to explain the XAS data in comparison to the visible femtosecond pump−probe data, which is fit satisfactorily by a simple sequential triexponential fit. Shown in Figure 4 is the summarizing Jablonski-type diagram from the TR-XAS data. Critically, we note that the time constants reported from femtosecond pump−probe data are not in accord with the time constants from TR-XAS. However, it is

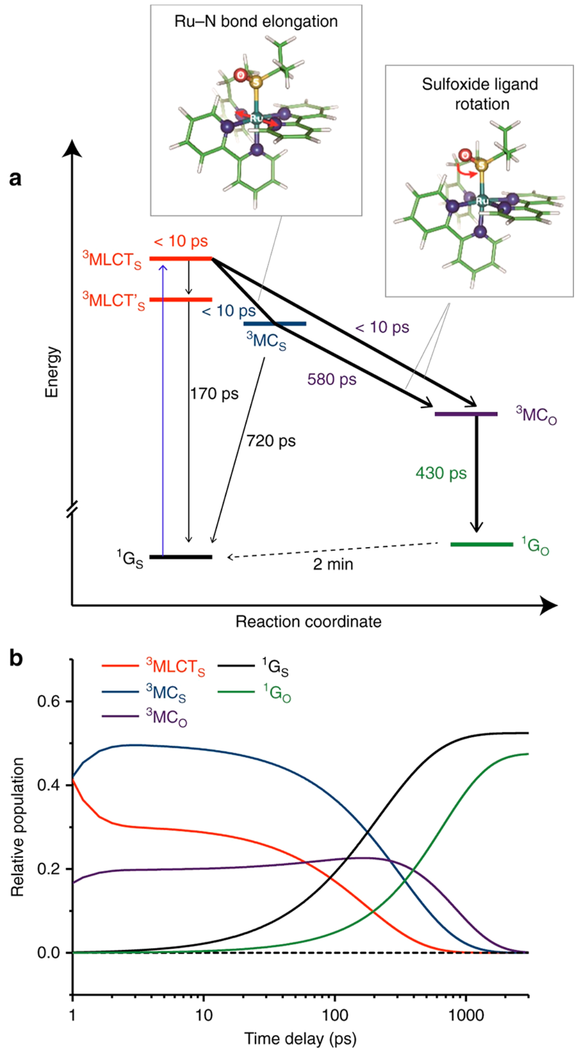


Figure 4. Proposed mechanism and kinetics for the photoisomerization of $[Ru(bpy)_2(pyESO)]^{2+}$. (a) Proposed photoisomerization mechanism with labels indicating electronic state and lifetime for each ground-state and intermediate structure. Bold arrows indicate the basic mechanistic requirements necessary to describe the Ru and S edge data, including the necessity of MC excited states (Ru edge) and two isomerization pathways (S edge), and the formation time for the O-bonded ground state. Insets show the major structural changes that accompany electronic transitions. (b) Time-dependent fractional population for each reaction intermediate. Adapted from ref 59.

not clear that they should be identical, as these two techniques are clearly measuring different spectral responses. As photochromic compounds show large structural rearrangements upon laser excitation, this technique promises to deliver an improved understanding of electronic−nuclear coupling. Moreover, as DFT methods continue to improve, we may gain an enhanced comprehension of excited-state bonding.

Photocrystallography has an important and notable history in the characterization of metastable linkage isomers of transition metal complexes containing NO,[60] SO_2,[61] and NO_2^-,[62] but its beginnings arise from irradiation of cinnamic acid to effect [2+2] cycloadditions,[63] which continues today.[64,65] Coppens led the way in these studies on sodium nitroprusside.[66,67] Separately, Cole has uncovered synergistic motions inside crystals of $[Ru(NH_3)_4(X)SO_2]^{n+}$ (X is typically an anionic or neutral ligand *trans* to SO_2), where the S-bonded SO_2 yields both η^2-SO_2- and O-bonded isomers upon irradiation of single crystals.[61,68−71] The relatively close packing of each Ru cation appears to cause other nearby cations to rotate. In this way, photonic energy is transduced to mechanical energy inside the crystal, reminiscent of a rotor.[70] The emergence of pulsed X-ray sources is certain to reveal other photophysical and photochemical mechanistic details. There are other dramatic mechanical and material effects that can be observed for other photochemical reactions.[72] Similarly, Raithby and co-workers have found metastable isomers of NO_2^- bound to Ni^{2+} in a variety of coordination environments.[62] An enduring challenge in this arena is that most of these transition metal complexes operate well below room temperature. Indeed, nitrosyl compounds, when irradiated at room temperature, liberate NO; they are thus often termed NO-releasing molecules (NORMs), which is its own very active area of research. There are also considerable challenges associated with collecting transient absorption data on single crystals (optical density, birefringence, local heating, catastrophic crystal damage, etc.), thus making comparison with single-crystal structural dynamics difficult.

One approach to overcome some of these obstacles is to collect transient absorption spectra on *suspensions* of nanocrystals of molecular compounds. Garcia-Garibay and co-workers have successfully applied laser flash photolysis to microcrystalline samples of organic compounds in an effort to correlate structural changes with kinetics.[51,53,73,74] In these studies, they were able to correlate structural rearrangements with two known self-quenching pathways.[75] As they have shown this approach to provide quality data on the femtosecond time scale, it would seem that this technique is ideally suited for photochromic compounds.

The application of TR-IR spectroscopy to photochromic complexes seems natural. A practical requirement of TR-IR is the presence of high extinction vibrations to probe. Transitions metal complexes often comprise CO or CN^- ligands, whereas many organic photochromes do not feature such functional groups. In principle, the combination of femtosecond visible pump−probe and infrared spectroscopies would yield remarkable insight into the photochemical mechanism. While they do not report time-resolved visible spectra, Burkey and Heilweil have reported extensively on the photochromic action of organometallic piano-stool-type complexes (e.g., $CpM(CO)_2$; M = Mn, Cr) by TR-IR.[76−82] In aggregate, these studies show dynamics of ν(CO) that correspond to bond-forming events of the metastable state on the order of 100 ps. This is in accord with the time scale for many transient visible events, and this underscores the importance of collecting and comparing both visible and atom-specific spectroscopy to learn more about excited-state evolution and excited-state bond-breaking and bond-making events.

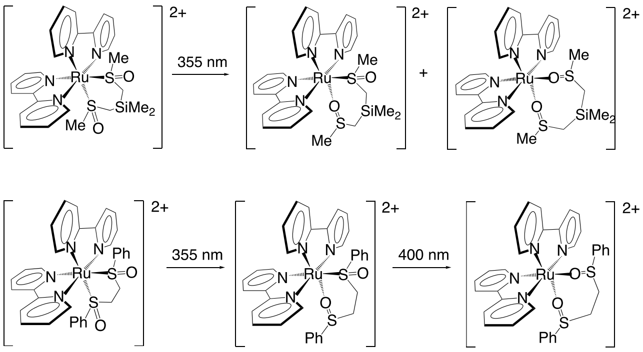
■ BIFURCATING SURFACES

A feature of all photochromic complexes is that they comprise excited-state surfaces that couple isomers with quite different molecular structures. These complexes then serve as excellent examples for studying how such surfaces connect and how nuclear motions are coupled to electronic surfaces and transitions. For photochromic compounds that contain more than one isomerizing unit, transient absorption spectroscopy can report on how the molecule moves along these surfaces, and how molecules respond to these intersection points. For many complexes, the result may simply be deterministic with respect to thermodynamics. However, recent studies have shown that certain reactions may be dynamically driven, such that the product ratio does not reflect thermodynamics.[83−87]

We have had a long-standing interest in ruthenium and osmium bis-sulfoxide complexes.[23,88] One motivation is to determine if multiple, seemingly orthogonal isomerizations can be triggered by a single photon absorption, or if two distinct excitations are required to prompt isomerization of both sulfoxide ligands. These complexes provide a complicated excited-state potential energy surface with nominal lowest energy CT (and LF) states that correspond to S,S-, S,O-, and O,O-bonded structures. Moreover, since these complexes exhibit C_2-symmetry in the ground state, questions emerge regarding which sulfoxide isomerizes first and if S,S→S,O→O,O reaction pathways are distinct from S,S→O,O reaction pathways.

Bulk photolysis and femtosecond probe spectroscopy revealed that $[Ru(bpy)_2(OSSO)]^{2+}$ (OSSO is dimethylbis(methylsulfinylmethyl)silane; Scheme 1, top) produced both S,O- and O,O-bonded isomerization products following excitation of the S,S-bonded ground state.[89,90] The reaction is both rapid and efficient, with an identical 250 ps time constant for formation of each product and an aggregate quantum yield of isomerization of 0.42. The O,O-bonded product yielded the S,S-bonded starting material thermally and proceeded in a sequential O,O→S,O→S,S fashion. This was evident from the presence of two temporally separated isosbestic points in the reversion spectra. Based on the thermodynamic ordering of the ground-state isomers, we initially assumed a similar ordering of the excited-state isomers

Scheme 1. Reactivity of $[Ru(bpy)_2(OSSO)]^{2+}$ and $[Ru(bpy)_2(OSSO)]^{2+}$.



and accordingly argued that all three exited-state structures must be in thermal equilibrium with one another. This mechanistic proposal allowed for the phototriggered formation of both S,O- and O,O-isomers and suggested a sequential relationship between the three isomers.

In contrast, our photochemical study of $[Ru(bpy)_2(bpSO)]^{2+}$ (bpSO is 1,2-bis(phenylsulfinyl)ethane; Scheme 1) revealed a one-photon absorption, one isomerization mechanism in solution.[91] Bulk photolysis UV−visible absorption spectra displayed two sets of isosbestic points, indicating that a ground-state S,O-isomer was formed from excitation of the S,S-isomer. Subsequent excitation of the S,O-isomer yielded the O,O-isomer. Pump−repump−probe transient absorption spectroscopy confirmed these results. These data indicated that there was no direct pathway for formation of the O,O-isomer from the S,S-isomer. If the excited-state structure was similar to that proposed for $[Ru(bpy)_2(OSSO)]^{2+}$, then at the very least the barriers separating excited-state S,S-, S,O-, and O,O-isomers were significantly greater. We reasoned that a less flexible chelate linker bridging the sulfoxides (OSSO: three-atom linker; bpSO: two-atom linker) would lead to the difference in barriers. However, in a gas-phase study of $[Ru(bpy)_2(bpSO)]^{2+}$ by ion mobility spectroscopy (IMS), we discovered that both S,O- and O,O-photoproducts were formed from irradiation of ground-state S,S-$[Ru(bpy)_2(bpSO)]^{2+}$.[92] These data demonstrate the importance of solvent in the reactivity of this complex.

Related to these complexes, Boggio-Pasqua performed a computational study on $[Ru(bpy)_2(dmso)_2]^{2+}$ (dmso is dimethyl sulfoxide) in order to address the presence of a one-photon, two-isomerization pathway (S,S→O,O), among other issues.[93] In this study, the results reveal that the photoisomerization can be achieved by either a one-photon or a two-photon mechanism, and that there appears to be a relatively smooth transition on the lowest energy potential energy surface from CT to MC (metal-centered). Moreover, the calculations reveal that there are a series of highly orchestrated motions that involve lengthening and shortening of both Ru−S bonds, lengthening and shortening of the Ru−N bond *trans* to each sulfoxide, and rotation of the sulfoxide, all prior to isomerization. Presumably, many of these distortions are also active or operative in chelating sulfoxides, such as in $[Ru(bpy)_2(OSSO)]^{2+}$ and $[Ru(bpy)_2(bpSO)]^{2+}$ (Scheme 1, bottom). In aggregate, we interpret these results to suggest that the excited-state potential energy surface is relatively soft and is strongly coupled to Ru−N bond-stretching, Ru−S bond-stretching, Ru−O bond-stretching, and sulfoxide rotation. Accordingly, we do not typically consider the ^{3}MC and ^{3}MLCT potential energy surfaces as separate but rather as one surface. The relative contribution of each electronic state at any one position on this surface reflects these Ru−N, Ru−S, and Ru−O bond distances. Viewed from the perspective of the atoms, as these distances and atoms rotate prior to and during isomerization, the energies of the ^{3}MC and ^{3}MLCT states are stabilized and destabilized relative to one another. We note that, in most cases, our femtosecond transient absorption data support the assignment of the lowest energy excited state as CT in character. However, this observation does not require that the ^{3}MC states are not mixed with the ^{3}CT states (as we describe above) or that they are not formally accessed during isomerization (assuming separation of MC from CT).

We recently revisited this complex to search for a bifurcation point along the lowest energy excited state.[88,94] Specifically, we challenged the notion of a sequential isomerization potential energy surface, where the energy of the S,O-isomer is always intermediate between those of the S,S- and O,O-states. We questioned if the potential energy surface is more correctly described by those motions that lead to single isomerization (S,S→S,O) being in fact separate from those that lead to double isomerization (S,S→O,O). In such a case, a view of an idealized potential energy surface may look similar to that in Figure 5.

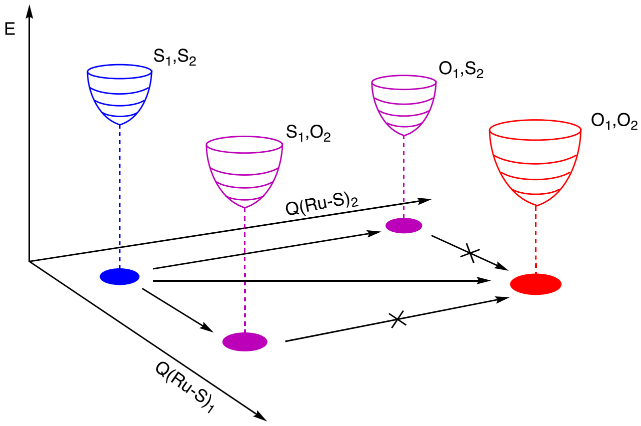


Figure 5. Depiction of ^{3}MLCT surface with minima corresponding to S,S- (blue), S,O- (purple), and O,O-bonded (red) isomers. The vertical axis is energy, and *x*- and *y*-axes represent the vibrations that lead to production of single isomerization products (S_1,O_2 and O_1,S_2). For bis-dmso (or bis-sulfoxide) complexes, there are two distinct reaction pathways (solid arrows) that designate production of single isomerization and double isomerization products. We see no evidence for direct conversion of an S,O- isomer to the O,O-isomer.

We show potential energy wells representing S,S- (blue), S,O- (magenta), and O,O-isomers (red) on the triplet excited-state surface. The surface comprises both ^{3}CT and ^{3}MC configurations, as described above. While we recognize that the ^{3}MLCT excited state is C_1-symmetric, the ground-state complex is C_2-symmetric, and it is not clear prior to excitation which sulfoxide will isomerize. Presumably, one sulfoxide is activated for isomerization following solvent reorganization and localization of the excited electron onto a single bipyridine. We propose two distinct S,O-isomers to reflect this difference. Since our spectroscopic studies do not reveal a direct, excited-state S,O- to O,O-isomer pathway, an arrow with an "x" denotes this absence of reactivity. Lastly, it is evident that as the molecule traverses this surface and moves away from the S,S-excited state it may encounter an intersection region in which the S,O-product is directed relative to the O,O-product. In this scenario, one might expect that alteration of the initial excited-state population would lead to changes in product yield.

Accordingly, we questioned if an excitation wavelength dependence would reveal changes in the quantum yields of isomerization (Φ_{SO} vs Φ_{OO}) and relative product yield. Indeed, this was observed and thus indicated two mechanistic possibilities: (1) coherence effects prompt different reaction profiles or (2) the initial excitation wavelength projects the initial excited-state population into different directions. Quantum control experiments were inconclusive, which was not unexpected since excited-state formation in $[Ru(bpy)_3]^{2+}$-type chromophores is solvent limited. If the projection hypothesis is accurate, then it suggests the presence of some space on the potential energy surface where the molecule "decides" whether to follow a one-isomerization pathway or two-isomerization pathway.

We performed pump−repump−probe (PRP) spectroscopy in hopes of identifying this interaction or bifurcation region. The role of the first pump wavelength is to prepare the excited-state population. The role of the repump pulse is to re-excite the initial excited-state population in order to alter the product yield. We reasoned that if the repump pulses coincided with the molecule traversing through this critical bifurcation region, then the product yield, product ratio, and quantum yield for each product would be altered. We chose 400 nm as the repump wavelength. This not only corresponds to an excited-state absorption in this class of molecules, but we have also long suspected the presence of a weak transition involving the sulfoxide at these wavelengths. By comparing the product yield, product ratio, and quantum yields of isomerization of the PRP experiment to the standard pump−probe measurement, we anticipated that we would identify when the excited-state population arrived at this critical bifurcation region. While we explored many experimental parameters (including low temperatures to rule out local heating effects), we found that regardless of the wavelength of the first pump excitation, a time delay (Δt) of 3.5 ps of the 400 nm repump wavelength significantly altered the outcome of the reaction. For example, with 355 nm pump, 400 nm repump, and 3.5 ps time delay, the [S,O]:[O,O] product ratio was 2.4, as compared to 1.8 when no repump was applied. Importantly, if the time delay separating pump and repump was too short (0.5 ps) or too long (675 ps), we observed little or no effect on the relative product distribution. These results suggest that the repump excitation coincides with excited-state evolution in this critical bifurcation region.

This study is ongoing, as it has prompted additional questions related to vibrational energy redistribution, transduction of photonic energy to potential energy, and the nature of excited-state potential energy surfaces. Moreover, this study has revealed that photochromic molecules can "map" excited-state potential energy surfaces to provide details not possible to observe in non-isomerizing chromophores. To date, there remain few bis-photochrome examples, and it would appear that these types of compounds would offer a construct to evaluate energy flow and energy conversion in molecular systems. These studies would be of interest to a broad range of researchers who have an interest in electron and energy transfer.

■ NEW AMBIDENTATE LIGANDS

The canonical structure of the sulfoxide ligand as an S═O functional group is misleading and should more correctly be viewed as a sulfoxide ylide ($S^+−O^−$). Such a view is more compatible with its reactivity. Indeed, thioethers are well-known O-atom acceptors, and sulfoxides are reactive as O-atom donors.[95] The ylide configuration allows one to consider other isoelectronic species as non-traditional ligands for the formation of bistable species. These include sulfimides and classical carbon−sulfur ylides (Figure 6).

Sulfimides (or sulfilimines) are relatively uncommon species in comparison to either sulfoxides or sulfonium ylides. Indeed, any comparative database search of sulfoxide versus sulfimide will yield *many* more responses for sulfoxide. Formal investigation of sulfimides originated in 1917 as a response to an emergent interest in compounds such as bis(2-chloroethyl) sulfide, more commonly known as mustard gas. Metazoan Collagen IV proteins feature the only known example of a naturally occurring sulfimide, where this linkage appears to be formed from reaction of lysine with methionine.[96] The sulfur−nitrogen ylide serves as structural reinforcement in the cross-linkages within animal tissues, in addition to acting as a ligand for cell-surface receptors. The juxtaposition between a structurally inert and a chemically responsive species makes the sulfimide a provocative candidate in designing dynamic transition-metal-based reactive species. Much of the research in this area is on the origin of the genetic coding for this linkage and much less on how this linkage affects the chemical and/or materials properties of skin. Nevertheless, a number of researchers have explored the creation and reactivity of these species.

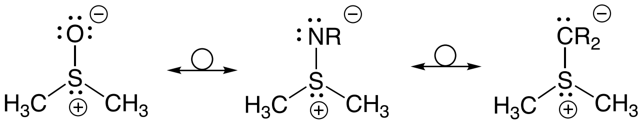


Figure 6. Structures of sulfoxide (left), sulfimide or sulfilimine (center), and carbon−sulfur ylide (right).

The coordination chemistry of sulfimides is relatively unexplored, with formal establishment in 1995 by Cramer et al. by way of the uranium-based complex, $[Cp^*_2UCl_2(Ph_2SNH)]$ (Cp* is cyclopentadienyl, and Ph_2SNH is *S,S*-diphenylsulfimide).[97] Nearly all subsequent reports have come from Paul Kelly's group at the University of Loughborough.[98−107] Their interest has been to develop new metal complexes to help understand the reactivity of this functional group and for use in the preparation of porous or framework material. In particular, the sulfimide ligand supports polymorphic crystal growth, leading to unusual birefringence, which is a consequence of crystal packing.[108] The potential of sulfimides as a reactive species was further revealed in a platinum-activated addition process, where the sulfimide was found inserted into a coordinated acetonitrile unit, forming a five-membered metallocycle, S,N-chelate (Figure 7). This complex is the only example of a sulfimide coordinating through the sulfur atom. To date, coordination of diphenylsulfimide to Ni^{2+}, Cu^{2+}, and Fe^{3+} has been exclusively shown to via N-bonding.[98−101,105,108] Nevertheless, it seems likely that through judicious choice of ancillary groups on sulfimide coordination to S can be engineered.

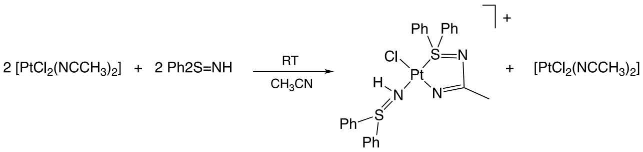


Figure 7. Platinum-activated addition of *S,S*-diphenylsulfimide to acetonitrile as reported by Kelly.[104]

Exhaustive work on organic sulfimides demonstrated how a dramatic range of physiochemical properties is attainable in response to altering the nature of the nitrogen's functional group. The potential of derivatizing the auxiliary nitrogen's substituent is a feature unique to the sulfimide and remains inaccessible to the isoelectronic sulfoxide group. Using this framework as a basis for ligand design, the sulfimide−metal bonding interactions could be modulated in a predictable manner, namely, by promoting preferential coordination to the metal center through nitrogen or sulfur. It stands to reason that a simple change of the sulfimide's functionality allows for a straightforward synthetic handle to aid in the efforts to develop a strong sulfur-donating ligand or even a ligand with dynamic coordination modes, S→N or N→S, analogous to its sulfoxide relative.

FIRST-ROW TRANSITION METAL COMPLEXES

While much photochemical research in this space is motivated by the creation of long-lived excited states with earth-abundant metals, we have questioned whether sulfoxide isomerization might allow for the photochemical generation and stabilization of higher or unusual spin states. For example, an iron complex featuring an S-bonded sulfoxide may exhibit a ground-state, low-spin state (^1A) that upon visible excitation forms an O-bonded metastable state that may stabilize triplet or quintet excited states. Such complexes would be of fundamental interest to understand the role of spin in isomerization reactions, as well as providing further insight into the nature of electronic−nuclear coupling.

While there are no examples of this type known to us, there are a number of literature reports that suggest sulfoxide isomerization on iron may lead to the stabilization of different spin states. For example, Scheidt has investigated iron-porphyrin sulfoxides and notes that in $[\mathrm{Fe^{III}(TPP)(tmso)_2}]^+$ (TPP is tetraphenylporphyrin; tmso is tetramethylenesulfoxide) the sulfoxide ligands are O-bonded and that in $[\mathrm{Fe^{II}(TPP)(tmso)_2}]^+$ the sulfoxide ligands are S-bonded.[109] Based on the $\mathrm{Fe^{II}}$−N distances to the porphyrin, (1.999(4) Å), these data strongly suggest that the complex is low spin. This is in accord with a number of other iron(II) porphyrin species with sulfur donors in the apical position. In contrast, bis-sulfoxide complexes of Fe(III) porphyrins are typically high spin. Thus, as described in Design Criteria, these complexes might be expected to show phototriggered sulfoxide isomerization behavior under the right conditions.

Randy Larsen has performed picosecond transient absorption studies on $[\mathrm{Fe^{II}(PPIX)(dmso)_2}]^{2+}$ (PPIX is protoporphyrin IX) and found evidence for a long-lived intermediate formed from photolysis.[110−113] Based on the bathochromic shift of the Soret transition, the photolytic intermediate is assigned as a five-coordinate, high-spin $\mathrm{Fe^{II}(PPIX)}$ featuring an S-bonded dmso ligand. The observed 100 ps transient absorption spectrum reveals a Soret that is consistent with a five-coordinate, Fe(II) porphyrin with imidazole or thiolate donors and dissimilar to Fe(II) heme phenolate species. These data suggest ligand loss and high-spin formation on a sub-100 ps time scale. Given the time scales of sulfoxide isomerization on ruthenium and intersystem crossing in Group 6 metals, it is not unreasonable to assume that isomerization of dmso yields a high-spin Fe(II) heme that is then labilized to produce the Larsen intermediate. Moreover, it may be that synthetic tuning of the porphyrin will generate a more stable ferrous heme sulfoxide.

This proposed reactivity might not be restricted to heme environments. Goldberg recently published a chelating sulfoxide based on tris(2-pyridyl)methylamine (tpa; Figure 8), and close inspection of the single-crystal X-ray data appears to show a disordered iron environment with both an S-bonded sulfoxide and an η^2-sulfoxide ($\mathrm{R_2S{=}O}$).[114] To our knowledge, this is the first example of any η^2-sulfoxide, though we previously proposed their existence in the phototriggered isomerization of dmso.[115] The photochemical reactivity was not addressed, but the crystal structure data prompt investigation of these and related complexes.

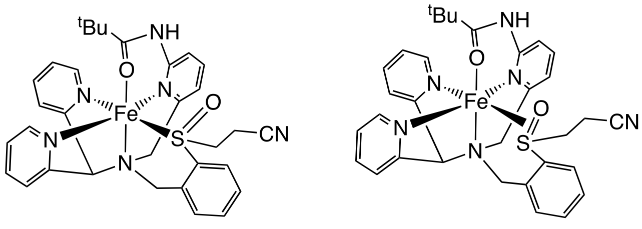


Figure 8. Bond-line structures of S-bonded and η^2-sulfoxide structures that correspond to molecular structures reported by Goldberg.[114]

Perhaps the first iron complex that featured phototriggered ligand isomerization was sodium nitroprusside, $\mathrm{Na_2[Fe(CN)_5(NO)]}$ (SNP). Beginning with the confounding assignment of the lowest energy visible transition as $\mathrm{Fe^{2+}}$ $d\pi \rightarrow$ NO $p\pi^*$ CT ($\varepsilon \approx 25$ $\mathrm{M^{-1}\ cm^{-1}}$),[116] this complex and its many derivatives were the subject of intense study and scrutiny, due to the production of colored metastable states in single crystals of this material when irradiated at low temperature.[117] At room temperature, this complex as well as many other nitrosyl complexes elease NO when irradiated. Ultimately, Coppens identified the metastable states as linkage isomers of the NO ligand by photocrystallography.[66,67] The ground state is unequivocally N-bonded, and he showed that MS1 (metastable state 1) was the O-bonded isomer and that MS2 (metastable state 2) was the η^2nitrosyl isomer. It is tempting to consider if this type of coordination environment might also support sulfoxide isomerization. With that in mind, we note a report of $[\mathrm{Fe(CN)_4dmso)_2}]^{2+}$ comprising a low-spin ferrous ion with S-bonded sulfoxides in a *trans*-configuration, similar to that found in hemes.[118] While no photochemical study was reported, the authors noted that the bound dmso ligand exchanged with dmso-d_6 within minutes of mixing at room temperature. Similar to SNP, it may very well be that irradiation of crystals of this complex at low temperature will exhibit isomerization.

CONCLUSION

The sections in this Perspective emphasize important experimental results as well as certain areas to be pursued in the future. By no means is this an exhaustive list, and there are other areas that are worthy of pursuit. In particular, computational methods are certain to aid our mechanistic understanding of these complicated reactions. These complexes can be readily incorporated into various molecular machine architectures, and this is an exciting area of research. In addition, photochromic compounds and complexes often display remarkable photomechanical effects in the right environment. Hopefully, the chemistry described here serves to inspire others in new and creative ways to continue work on photochromic compounds of all types.

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Notes

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