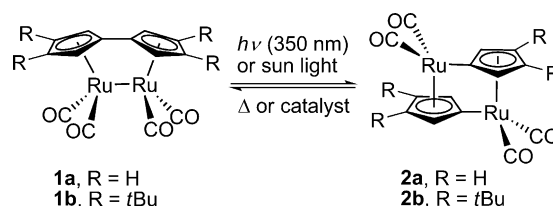


X-ray Transient Absorption and Picosecond IR Spectroscopy of Fulvalene(tetracarbonyl)diruthenium on Photoexcitation**

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In the burgeoning efforts of collecting solar energy for power generation,^[1] the development of rechargeable solar thermal batteries containing photochromic molecules capable of reversible photoisomerization is receiving increasing scrutiny.^[2] Among them, organometallic compounds show particular promise, because of their complementary potential for steric and electronic tunability.^[3] In this regard, an intriguing system with which to illustrate the concept is the robust photothermal fulvalene (Fv) diruthenium couple **1**⇌**2** (Scheme 1).^[4] Initially assumed to occur by a concerted pathway, a recent study of the heat releasing step **2a**→**1a** pinpointed a stepwise trajectory. Its salient features (Figure 1, black solid line) consist of a pre-equilibrium of **2a** (20.8 kcal mol⁻¹) with anti biradical **B** (38.8 kcal mol⁻¹) by initial cyclopentadienyl (Cp) coupling (transition state, TS, **C**, 43.2 kcal mol⁻¹), subsequent rate-determining CpRu(CO)₂ rotation (TS **A**, 50.5 kcal mol⁻¹), and Ru–Ru bond formation to give **1a** (0.0 kcal mol⁻¹).^[5] The relative difficulty of anti to syn biradical rotation and the ease with which **B** proceeds to **2a**



Scheme 1. Photoisomerization of fulvalene(tetracarbonyl)diruthenium at ≥ 350 nm and its thermal reversal. Irradiation ≤ 300 nm causes decarbonylation.^[4a]

($\Delta H^\ddagger = 4.4$ kcal mol⁻¹) prompted a reconsideration of the mechanism of the photostorage step. Originally,^[4a] the normally expected Ru–Ru photodissociation^[6] was discounted, because added CCl₄ (1M) had no effect on the outcome of the photorearrangement, leading again to the postulate of a concerted process. However, the effortless step **B**→**2a** makes **B** a viable photointermediate, provided that it

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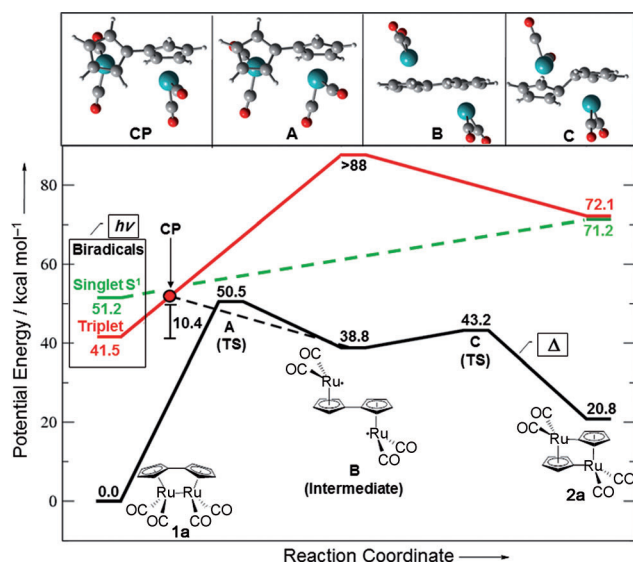


Figure 1. Calculated potential-energy profiles for the thermal $2a \rightarrow 1a$ manifold (black solid line), two biradical species obtained by photoexcitation of **1a** (box left), and the computed fate of these species (excited-state triplet in red, singlet in green; CP = crossing point).^[8] Computer-rendered depictions of A–C and the CP are shown at the top. Higher excited states are omitted.

can be reached by relaxation of an excited state of **1**. Moreover, if the result of photon absorption is indeed intermetallic cleavage, the question arises of how the system overcomes the syn to anti rotational barrier. The following experiments, executed with the relatively soluble tetra-*tert*-butyl derivative **1b**^[4b] and related computationally to the unsubstituted analogue **1a**^[5] (the core structures are relatively unperturbed by the *tert*-Bu substituents),^[4b] address these issues and provide a coherent picture of the photoconversion of **1** to **2**.

We have sought direct structural knowledge of the reactive transients by X-ray transient absorption (XTA) spectroscopy, which has been established^[7] as a technique capable of probing local metal center coordination geometry on a time scale limited mainly by the durations of X-ray pulses from a synchrotron or other light sources. The XTA measurements were performed at Beamline 11-ID-D of the Advanced Photon Source at Argonne National Laboratory. Details of this setup have been published.^[7,8] Briefly, in a manner analogous to optical transient absorption, an ultrafast, 351 nm laser excitation pulse is used to initiate the reaction, and an X-ray pulse of about 100 ps duration, tuned to an energy around the Ru K-edge (22.117 keV), is applied to obtain the spectrum of the transient excited state at 100 ps time delay. Spectra of **2b** were obtained after maximum conversion of **1b** by long exposure (ca. 8 h) to the optical excitation.

The X-ray absorption near-edge structure (XANES) region of the XTA results is shown in Figure 2. The XANES region is sensitive to the electronic state and coordination geometry of the X-ray absorbing ruthenium. In control experiments, distinct differences are seen between the ground state (GS) spectra (without optical excitation) of **1b** and its photoisomer **2b**. On laser illumination (LI) of **1b**,

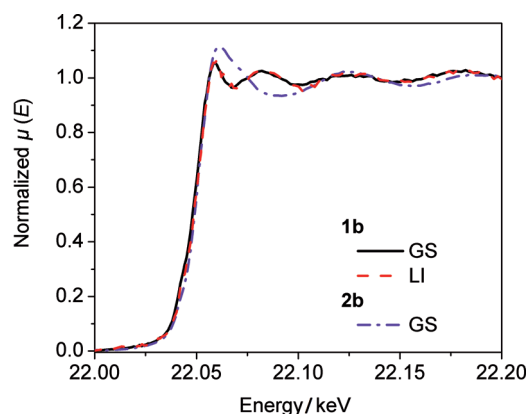


Figure 2. Ru K-edge XANES spectra of **1b** and photoisomer **2b** in the ground state (GS) and the spectrum of laser illuminated **1b** (LI); $\mu(E)$ = normalized X-ray absorption amplitude.

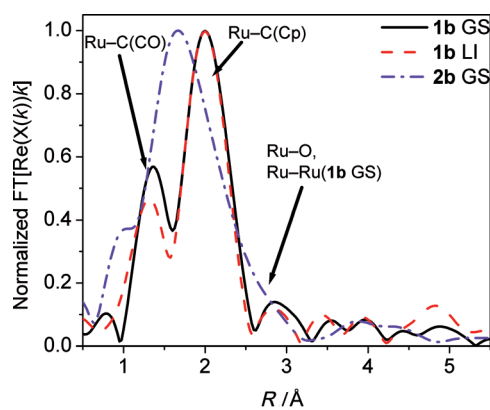


Figure 3. Normalized Fourier transform of the XAFS spectra of **1b** before (GS) and after laser illumination (100 ps delay; LI), and of **2b** (GS). Each peak represents the average distance (not phase-corrected) of neighboring atoms (arrows) from the absorbing Ru (Cp = attached cyclopentadienyl). Spectra are not corrected for phase shifts.

subtle changes are noted, which become more apparent in the Fourier-transformed X-ray absorption fine structure (XAFS) spectra (Figure 3). While the absorptions of the GS of **1b** and LI are similar in shape, the ratio between the amplitudes of the 1st and 2nd peaks (the former due to scatter from Ru–C(CO), the latter to Ru–C(Cp) and multiple scattering events) varies. The large distribution of Ru–C distances is reflected in the broad peak observed in the Fourier-transformed data for **2b**.

Employing the computed structures for the **1a/2a** manifold,^[5] Fourier-transformed XAFS data were fit to Equation (1),^[9]

$$\chi(k) = \sum_i F_i(k) S_0^2(k) N_i / (k R_i^2) \exp(-2\sigma_i^2 k^2) \sin[2k R_i + \phi_i(k)] \quad (1)$$

in which $F(k)$ is the magnitude of the backscattering, S_0 the amplitude reduction factor, N the coordination number, R the average distance, σ^2 the mean-squared displacement, and ϕ_i the phase shift; the subscript indicates the i th atom, k the electron wavevector.^[8] The results are shown in Figure 4. The

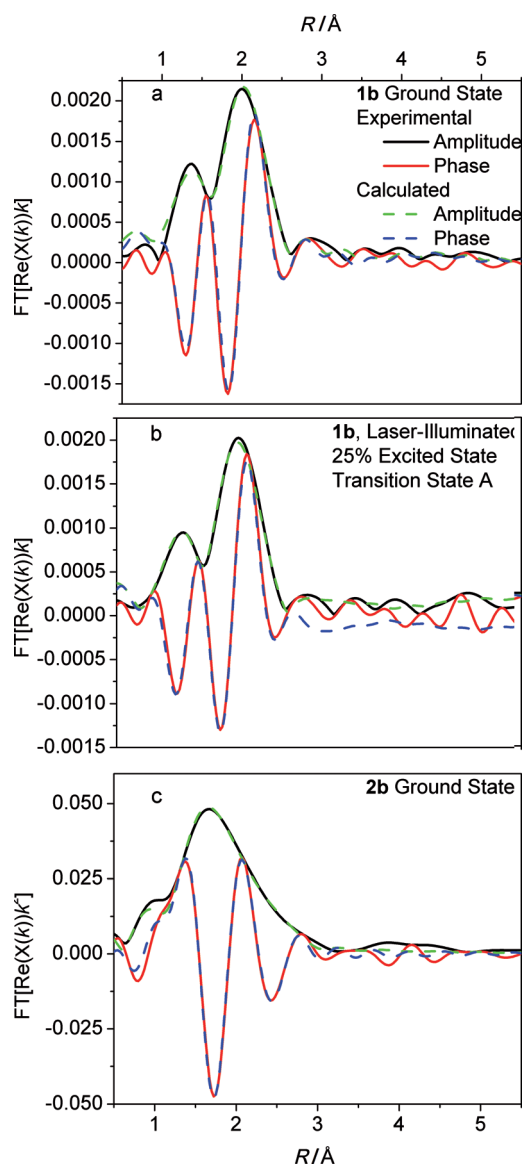


Figure 4. Fourier-transformed XAFS spectra for (top to bottom) **1b**, laser-illuminated **1b**, and photoisomer **2b**. Calculated results are based on computed structures. Spectra are not corrected for phase shifts.

ground-state XAFS data for **1b** and **2b** were well-fit using the computed structures of their respective analogues **1a** and **2a**. The data for laser-illuminated **1b** (LI) could be best fit by a combination of the ground state **1b**(GS), necessary to account for unexcited material present, and one intermediate species. Using more than one transient structure could not be justified because of the limiting signal-to-noise ratio of the measurements. Hence, we chose for this purpose the structures of intermediate **B** and the topologically extreme transition states **C** and **A**.^[5] The contribution of these species was varied relative to **1b** from 0 (all **1b**) to 60%. Structures **B** and **C** failed to produce satisfactory scattering profiles at any ratio,^[8] while **A** fared significantly better, with a best fit obtained at 25% **A** and 75% **1b** (Figure 4b). Even with the caveat of the signal to noise ratio limitations, it is clear that

optical excitation of **1b** generates an entity in which the Ru–Ru linkage is ruptured and which is not **B**, **C**, or **2b**, suggesting the formation of a Ru-centered biradical with a syn configuration.

To obtain additional information about the primary product of photon absorption, picosecond time-resolved infrared (TRIR) spectroscopy experiments were executed, following the course of the excitation of **1b** in heptane with 267 and 400 nm laser pulses, respectively.^[8] In general, for dinuclear metal carbonyl compounds,^[9] the former regime elicits CO loss (as observed for **1a**),^[4a] the latter M–M bond cleavage (for **1a**, rearrangement).^[4a] With 400 nm light, new absorptions emerge at early delay times (< 100 ps), which are relatively broad and dominated by a single species, but, as the latter decays, additional photoproducts become visible. Specifically, there are two sets of kinetically correlated peaks: one (**D**) comprising signals at 1945, 1995, and 2010 cm^{−1}, decaying with a time constant of about 30 ps, and a second (**E**), composed of bands at 1933 and 1970 cm^{−1} and more persistent, up to about 2 ns (Figure 5). Both **D** and **E**

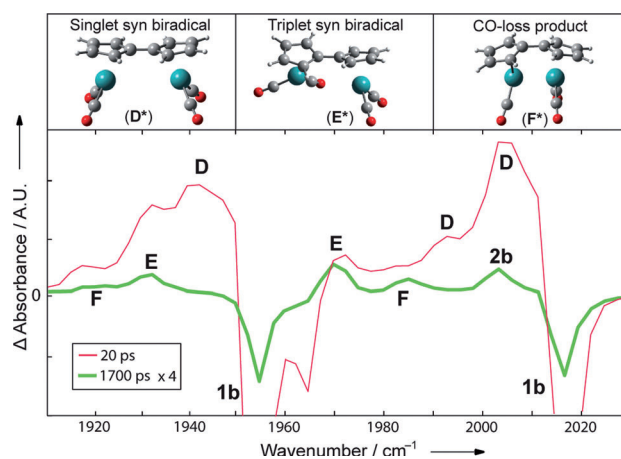


Figure 5. TRIR spectra of **1b** in heptane following 400 nm excitation. The structures depicted on top were computed for the unsubstituted analogues (*), FvRu₂(CO)₄ (**D*** and **E***), and FvRu₂(CO)₃ (**F***), using the BP86 functional and the lan12dz basis for Ru and the 6-31g(d,p) basis for all other atoms.^[8]

disappear on the picosecond timescale correlated to the recovery of **1b**, which is consistent with the formation of transient biradicals capable of rapid recombination to the starting material.^[6,10] Since this behavior rules out the creation of *tert*-butyl **B** (which should go on to **2b**; Figure 1), and guided by the XTA data, we assign the entity with the faster decay to a singlet syn biradical photoproduct **D**, and the other to its long-lived triplet relative **E**. For comparison, the analogous near-UV photolysis (> 375 nm) of [CpRu(CO)₂]₂ produces the CpRu(CO)₂ radical with IR bands at 1930 and 2000 cm^{−1}.^[11] The considerably weaker intensity of absorptions corresponding to **E** suggests that the primary pathway for the decay of **D** is to reform **1b**, although relaxation to the more stable triplet **E** is a likely competing pathway. As expected,^[4a] when the experiment is carried out with 267 nm excitation, monodecarbonylation to (*tert*-

$(\text{Bu})_4\text{FvRu}_2(\text{CO})_3$ **F** is observed,^[8] as evidenced by signals at 1910, 1922, and 1985 cm^{-1} . These absorptions reasonably match computed values for the parent $\text{FvRu}_2(\text{CO})_3$ **F*** (1927, 1941, and 1993 cm^{-1} ; intensities in agreement with experiment) and those reported for $(\text{CpRu})_2(\text{CO})_3$ (1935, 1964, and 1997 cm^{-1}).^[11] Much smaller amounts ($<1\%$) of species **F** appear to be formed at 400 nm (Figure 5). Finally, a weak absorption at 2004 cm^{-1} is assigned to traces of isomer **2b**^[8] (authentic sample^[4b] $\tilde{\nu}_{\text{film}} = 1932$ and 1993 cm^{-1}). To obtain further information about **D** and **E**, DFT was again applied to the parent analogues **D*** and **E*** (Figure 5 top). Of the two entities, only **E***, 41.5 kcal mol^{-1} more energetic than **1a**, provided a stable local minimum with $\tilde{\nu}_{\text{calcd}} = 1945$, 1990, and 2003 cm^{-1} , in agreement with experiment (for the two observable bands). Its topology features an intermetallic distance of 4.530 Å and a dihedral angle around the Cp–Cp bond of 37.53°. The “stability” of **E** in silico is consistent with its longer lifetime in solution relative to **D**. While the high spin–orbit coupling expected for a Ru complex should facilitate interconversion between spin states, there appears to be a small enthalpic barrier to reaching the crossing point from **D** to **E**.^[12] Because optimization of a singlet syn biradical structure led to collapse to **1a**, for purposes of illustration an artificial topology was modelled by inserting butane into the Ru–Ru bond and subsequently deleting the solvent molecule.^[13] The resulting **D*** has a Ru–Ru separation of 4.790 Å and a dihedral angle around the Cp–Cp bond of 1.51°. In short, TRIR confirms the rupture of the Ru–Ru bond as the primary step of the photoconversion of **1** to **2** and the formation of a relatively stable triplet biradical species.

How do any of the postulated intermediates reach photoisomer **2**? To answer this question, we resorted to first-principles DFT calculations using the methodology applied in the elucidation of the mechanism of the thermal reversal of **2a** to **1a** (Figure 1, black solid line).^[5] Mapping minimum-energy paths from the excited singlet or triplet electronic states indicated endothermic trajectories (Figure 1, green and red line, respectively).^[8] However, starting from the triplet **E***, a crossing point (CP) to the singlet surface on route to **2a** could be located at 10.4 kcal mol^{-1} , allowing access to intermediate **B** (Figure 1, black dashed line), from which further isomerization to **2a** is facile.^[5] The topology of the CP, with a Ru–Ru separation of 4.270 Å and Cp–Cp dihedral angle of 85.87°, is similar to that of TS **A** for syn–anti isomerization of the biradical. It thus appears that the primary step in the mechanism of the photostorage step **1**→**2** is a “classical”^[9] metal–metal bond dissociation. However, the resulting triplet syn biradical faces a thermal hurdle before it can proceed via **B** to the product.

The above postulate prompted additional preparative experiments. To confirm the absence of polar excited states or intermediates, the relative extent of conversion of **1b** to **2b** was monitored in hexane, heptane, toluene, and tetrahydrofuran (THF), respectively [$h\nu$, 350 nm, aqueous NaNO_2 (75 % w/v) filter, 1 min, 30°C], revealing little variance (relative ratios of **2b**:**1b** = 3.9:3.8:2.7:1.0), consistent with the emerging mechanistic picture. A second, more telling study addressed the presence of a CP that requires 10.4 kcal mol^{-1} of thermal activation to be reached from **E** on the way

to **2b**. The intervention of such a barrier was indeed corroborated by the discovery of temperature dependence of the photoconversion of **1b** to **2b** [9.3 mm in toluene, $h\nu$, 350 nm, aqueous NaNO_2 (75 % w/v) filter, 5 min]. Whereas at 40°C there was 20 % conversion, this number decreased steadily on lowering the temperature (e.g. 20°C, 11 %; 0°C, 6 %; –20°C, 3 %; –60°C, 0 %). Thus, low-temperature photolysis renders the ensuing syn biradical unproductive with respect to isomerization to **2b**, suggesting that it may be trappable. Indeed, while prolonged irradiation (100 min) of **1b** at –38°C in THF gave only 5.4 % conversion to **2b**, added CCl_4 (1:1 v/v) caused 31 % of **1b** to disappear to engender cleanly two new compounds, namely the conventional chloride abstraction product **3**^[5,10] and the novel adduct **4**, bearing a demetallated, trichloromethylcyclopentadiene ring (Figure 6), in addition to **2b** (ratio = 20:7:3). A control

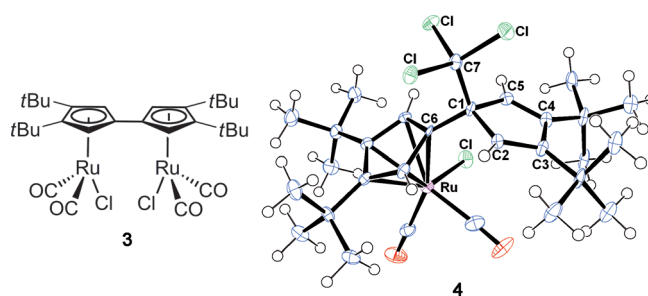


Figure 6. Products **3** and **4** (structure confirmed by X-ray crystallographic analysis)^[15] of the low-temperature irradiation of **1b** in the presence of CCl_4 . Selected bond lengths [Å] and angles [°] for **4** (one of two molecules in the unit cell): Ru–Cp_{centroid} 1.871, Ru–Cl 2.4113(12), C1–C6 1.512(6), C1–C2 1.506(6), C2–C3 1.343(6), C3–C4 1.526(6), C4–C5 1.345(6), C1–C5 1.493(6), C1–C7 1.566(7), C7–Cl_{average} 1.781.

showed that **3** is stable under the conditions of its generation and not a precursor to **4**. While anti biradical **B** generated thermally from **2b** (CCl_4 , 70°C),^[5,8] also produces **3**, its intervention is ruled out not only by the low-temperature conditions, but also by the absence of **4** in this experiment. We speculate that the emergence of this unique addition product is the result of the syn conformation of the diruthenium species, which facilitates the capture of $\cdot\text{CCl}_3$ by the second $\text{CpRu}(\text{CO})_2$ unit after initial abstraction of Cl[•] from CCl_4 by the first, probably in the solvent cage.^[14] These data complement the mechanistic picture painted by the other techniques brought to bear on this problem.

In conclusion, a combined picosecond transient X-ray and IR spectroscopic, DFT computational, and laboratory time scale experimental study has elucidated the mechanism of the photostorage step in the thermally reversible isomerization of **1** to **2**. It encompasses fast Ru–Ru bond cleavage to both singlet and triplet syn biradicals, the latter one of which proceeds to photoisomer **2** via a triplet–singlet crossing point to furnish anti biradical **B** by Cp–Cp rotation. Thus, neither process—photoisomerization and thermal reversal—are concerted, as proposed originally, but involve biradical intermediates. The unique dynamics of this system are controlled by the sizeable barrier to rotation around the Fv single bond,

which frustrates the optical by a coupled thermal activation step, and which enforces a pre-equilibrium between **2** and its anti biradical in the thermal release process. These insights are proving valuable in the design of improved systems and in the assembly of a functioning device.^[16]

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