samples of **3** under argon at room temperature turned cloudy after several days, but major decomposition did not occur. It is evident that **3** is rather stable thermally, although it is highly reactive toward common reagents.

Our studies in this area are continuing with emphasis on the preparation of other silacyclopropenes and on a broad scope study of the chemical reactivity of this novel class of compounds. It will be of special interest to determine if the trimethylsilyl substituents play an important role in the stability of **3**. We were prompted to disclose these preliminary results by a paper presented at the 10th Organosilicon Award Symposium by Gaspar and Conlin[12] in which the synthesis of tetramethylsilirene by the flow pyrolysis of 1,2-dimethoxytetramethyldisilane in the presence of 2-butyne was claimed.

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Dietmar Seyferth,* Dennis C. Annarelli, Steven C. Vick
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Electron-Transfer Reactions of Excited States: Direct Evidence for Reduction of the Charge-Transfer Excited State of Tris(2,2′-bipyridine)ruthenium(II)

Sir:

The charge-transfer excited state of tris(2,2′-bipyridine)ruthenium(II) ($*Ru(bpy)_3^{2+}$)[1] is a more powerful reducing agent (eq 1) than the ground state molecule by ~2.1 V, the excitation free energy.[2,3] Thus oxidants (e.g., $Co^{III}(NH_3)_5X^{2+}$,[2,4] Fe^{3+},[5–7] $Ru(NH_3)_6^{3+}$ [2,6]) can quench the emission from $*Ru(bpy)_3^{2+}$ by an electron-transfer mechanism (eq 2) as has been demonstrated by product analyses,[4] steady-state measurements,[7] flash-photolysis experiments,[6] and rate comparisons.[2,3,7]

$$Ru(bpy)_3^{3+} + e \rightleftharpoons *Ru(bpy)_3^{2+}, \quad E^0 = -0.83\,V \qquad (1)$$

$$*Ru(bpy)_3^{2+} + Q \longrightarrow Ru(bpy)_3^{3+} + Q^- \qquad (2)$$

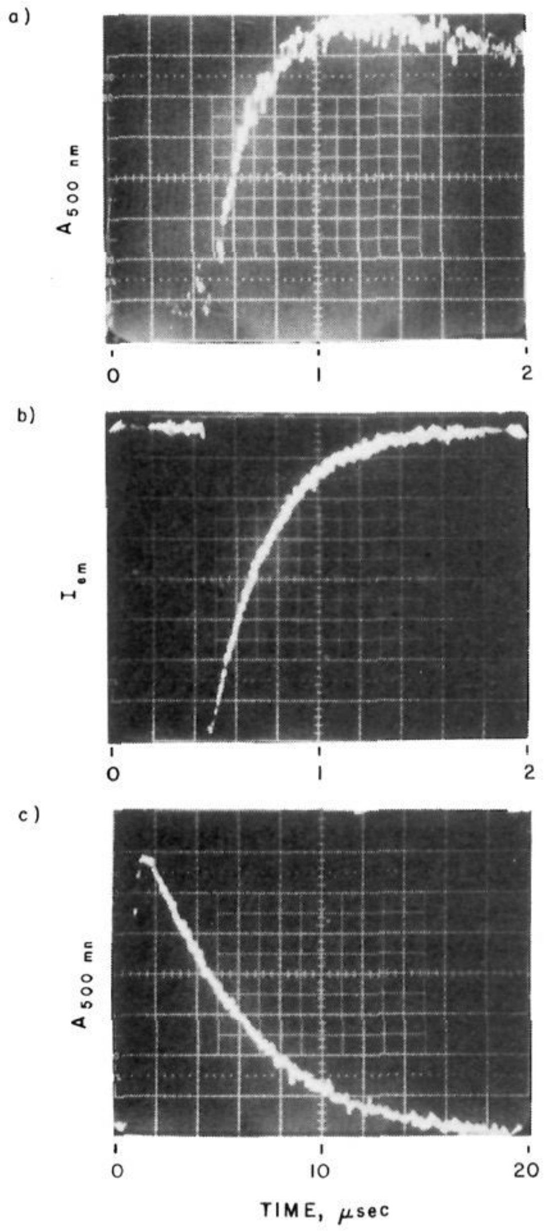

Figure 1. Flash photolysis of europium(II)–$Ru(bpy)_3^{2+}$ solution: (a) absorbance at 500 nm ($\Delta A \sim 0.02$ per major division) as a function of time (0.2 μs per major division); (b) emission intensity at 600 nm (I_{em} increases *down* the trace) in arbitrary units as a function of time (0.2 μs per major division); (c) same as (a), but 2 μs per major division.

The same excited state is also expected to possess oxidizing properties (eq 3). Evidence for reduction of $*Ru(bpy)_3^{2+}$ (eq 4) to $Ru(bpy)_3^+$ (which has previously been produced by

$$*Ru(bpy)_3^{2+} + e \rightleftharpoons Ru(bpy)_3^{+}, \quad E^0 = +0.84\,V \qquad (3)$$

$$*Ru(bpy)_3^{2+} + Q \longrightarrow Ru(bpy)_3^{+} + Q^+ \qquad (4)$$

electrochemical[8,9] and pulse-radiolysis[10] techniques) has recently been sought by studying the quenching of the $*Ru(bpy)_3^{2+}$ emission by reductants such as Eu(II),[11] $Ru(NH_3)_6^{2+}$ [11] and metal cyanides (e.g., $Os(CN)_6^{4-}$).[12] Here we present results of flash-photolysis experiments which provide direct evidence for the reduction of the charge-transfer excited state to $Ru(bpy)_3^+$.

Flash-photolysis studies using a frequency-doubled neodymium laser as the excitation source[7b] (λ 530 nm, pulse width ~30 ns) were undertaken for the Eu^{II}–$Ru(bpy)_3^{2+}$ system[11] (Eu(II) 0.01–0.1 M; $Ru(bpy)_3^{2+}$ $0.3\text{–}3 \times 10^{-4}$ M; excitation intensities $10\text{–}10^2$ einstein $cm^{-2}\,s^{-1}$; 0.5 M Cl^-, 0.05 M H^+, 25 °C). Examples of the traces obtained are shown in Figure 1. An increase in absorbance in the region 470–550 nm (Figure 1a) accompanied the decrease in emission intensity following the excitation flash (Figure 1b). The magnitude of the absorbance increase at 500 nm was linear in the excitation light intensity. The rate of decay of the transient (Figure 1c) was first-order in the transient and first-order with respect to added Eu(III).[13] These observations are interpreted in terms of the following sequence: reductive quenching of $*Ru(bpy)_3^{2+}$ to yield $Ru(bpy)_3^+$ and Eu(III) (eq 6, Figure 1a) is followed by Eu(III)-oxidation of $Ru(bpy)_3^+$ to regenerate the preflash

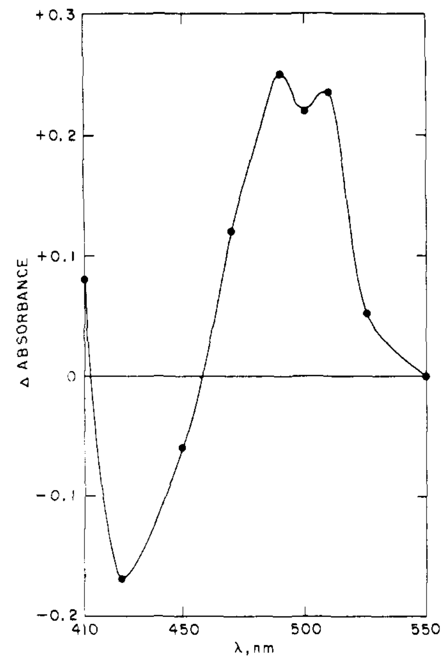

Figure 2. Difference spectrum for $Ru(bpy)_3^+$-$Ru(bpy)_3^{2+}$: 0.08 M Eu(II), 1.4×10^{-4} M $Ru(bpy)_3^{2+}$, 0.5 M Cl^-, 0.05 M H^+, 25 °C, 10 nm band pass for probe beam.

solution absorbance (eq 7, Figure 1c). At 25 °C, $k_q = 2.8 \times 10^7\ M^{-1}\ s^{-1}$ [11] and $k_7 = 2.7 \times 10^7\ M^{-1}\ s^{-1}$.

$$Ru(bpy)_3^{2+} \underset{1/\tau_0}{\overset{\lambda\ 530\ nm}{\rightleftharpoons}} {}^*Ru(bpy)_3^{2+} \tag{5}$$

$$^*Ru(bpy)_3^{2+} + Eu(II) \xrightarrow{k_q} Ru(bpy)_3^+ + Eu(III) \tag{6}$$

$$Ru(bpy)_3^+ + Eu(III) \xrightarrow{k_7} Ru(bpy)_3^{2+} + Eu(II) \tag{7}$$

The difference spectrum obtained for the transient is presented in Figure 2. The spectrum was the same at 0.05 M H^+ (shown), 0.4 M H^+, and pH 3. The same transient is produced in smaller yields from reaction of $^*Ru(bpy)_3^{2+}$ with $Ru(NH_3)_6^{2+}$ and $Fe(CN)_6^{4-}$. In addition, 500-nm-absorbing transients are produced when solutions containing Eu(II) and RuL_3^{2+} (L = 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, 4,7-dimethyl-1,10-phenanthroline, and 5-chloro-1,10-phenanthroline) are flash photolyzed. Detailed observations for the latter systems will be reported elsewhere. Figure 2 is similar to, but not identical with, the spectrum reported by Baxendale and Fiti.[10] The reduced species which they generated by reaction of $Ru(bpy)_3^{2+}$ with e_{aq}^- or Zn^+ has λ_{max} 510 nm (ϵ $1.2 \times 10^4\ M^{-1}\ cm^{-1}$), 530 nm (here 490, 510 nm) with a second, less intense, maximum at ~610 nm which we do not observe. Using the reaction of $^*Ru(bpy)_3^{2+}$ with Fe^{3+} (yield of $Ru(bpy)_3^{3+} + Fe^{2+}$, 0.8 ± 0.2[7]) to estimate the initial post-flash concentration of $^*Ru(bpy)_3^{2+}$, allowing for the fraction of excited state quenched, and assuming a yield of 1.0 for reaction 6, the molar absorptivity of $Ru(bpy)_3^+$ at 490 nm is calculated to be $(1.4 \pm 0.3) \times 10^4\ M^{-1}\ cm^{-1}$. Thus in intensity and band shape the visible spectrum of $Ru(bpy)_3^+$ strongly resembles that of $Ru(bpy)_3^{2+}$,[1a] and it is possible that the 490–510-nm band in the spectrum of $Ru(bpy)_3^+$ (like the 450-nm band for $Ru(bpy)_3^{2+}$) is associated with a metal-to-ligand charge-transfer ($d^6(\pi^*)^1 \rightarrow d^5(\pi^*)^2$) transition.[14]

There is now ample evidence that the charge-transfer excited state of $Ru(bpy)_3^{2+}$ readily undergoes both oxidation and reduction, as is predicted from thermodynamic and spectroscopic considerations.[2,11] One additional implication of such considerations can be seen by subtracting eq 1 from eq 3 to give eq 8. Disproportionation of the excited state (eq 8) is thus estimated to be favored by ~1.7 V. Evidence for the occurrence of reaction 8 is presently being sought at high $Ru(bpy)_3^{2+}$ concentrations and high light intensities.

$$2{}^*Ru(bpy)_3^{2+} \rightleftharpoons Ru(bpy)_3^{3+} + Ru(bpy)_3^+ \tag{8}$$

The flash-photolysis technique described here thus offers a convenient means of probing the chemistry of both the excited state $^*Ru(bpy)_3^{2+}$ and the unstable oxidation state $Ru(bpy)_3^+$. Fundamental studies of this kind may also be of considerable practical import in solar energy conversion as complexes like $Ru(bpy)_3^{2+}$ have properties which make them useful mediators in the photodissociation of water.[15,16]

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(13) Even in the absence of added Eu(III) the decay of the transient remained exponential ($\tau \leqslant 50\ \mu s$) rather than displaying second-order kinetics as expected from eq 7. A second-order decay is expected on other grounds, as well, since Baxendale and Fiti report that $Ru(bpy)_3^+$ undergoes reaction with itself with a rate constant of $3.5 \times 10^8\ M^{-1}\ s^{-1}$.[10] The absence of second-order behavior is attributed to the fact that the small amounts (10^{-4}–10^{-3} M) of Eu(III) unavoidable as an impurity in Eu(II) solutions raise the Eu(III) concentration to well above the post-flash $Ru(bpy)_3^+$ concentration ($\leqslant 10^{-5}$ M). Consequently k_7[Eu(III)] is always $> 3.5 \times 10^8$ $[Ru(bpy)_3^+]$ so that reaction 7 predominates and follows pseudo-first-order kinetics under all conditions.

(14) By contrast, the lowest energy absorption maximum for $^*Ru(bpy)_3^{2+}$, which like $Ru(bpy)_3^+$ has one electron in the ligand π^* system but only five metal d electrons, occurs at ~360 nm (C. Creutz, unpublished observations, 1975). A referee has suggested that the assignment $d^6(\pi^*)^1 \rightarrow d^7$ for the 490–510-nm band of $Ru(bpy)_3^+$ may more readily account for the positions of the band maxima in $Ru(bpy)_3^+$ and $^*Ru(bpy)_3^{2+}$. Although this assignment is not unreasonable on energetic grounds, the band seems remarkably intense ($\epsilon > 10^4\ M^{-1}\ cm^{-1}$) for this kind of transition.

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Carol Creutz,* Norman Sutin

Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

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Homoallylic[1] Interaction Involving Nitrogen Lone Pairs, a Reexamination

Sir:

Recently published work has examined the significance of homoallylic interaction between a nitrogen lone pair and a remote π bond in bicyclic amines.[2-5] Comparison with data from well-established model systems led us to reassign the photoelectron spectra (PES) of the bicyclic amines **5–8** of ref 2a and hence challenge the reported conclusions regarding the importance of homoallylic interaction in such systems. The recent report[5] of the NMR data for **5–8** confirmed our skep-