The residue is pure *cis*-**6** which melts (decomposition) at 49–50°. Although solutions of this azo compound are unstable above 10°, once the solvent has been removed the crystalline solid may be handled routinely for short lengths of time at room temperature. It is stable indefinitely if kept in the dark at −20°: nmr ($CDCl_3$) $\delta$ 1.58 (6 H, s), 6.20 (2 H, m), 7.0–7.4 (8 H, m); visible (octane) $\lambda_{max}$ 435 nm ($\epsilon$ 273); ir (KBr) 1550 $cm^{-1}$.

***cis*-1-(2-Phenyl-2-butyl)-2-phenyldiazene.** The exact same procedure yields a yellow oil which decomposes neat above 5°. It has moderate stability when stored at −20° in the dark (1 week): nmr ($CDCl_3$) $\delta$ 0.92 (3 H, t), 1.27 (3 H, s), 2.52 (2 H, q), 6.15 (2 H, m), 7.0–7.4 (8 H, m); visible (octane) $\lambda_{max}$ 435 nm ($\epsilon$ 279).

***cis*-1-*tert*-Butyl-2-phenyldiazene.**[39] The above procedure yields *cis*-**8** as a yellow oil. It returns to trans slowly at room temperature but it is stable indefinitely at −20° in the dark; visible (octane) $\lambda_{max}$ 420 nm.

***cis*-1-$\alpha$,$\alpha$-Dimethylallyl-2-phenyldiazene.** The standard procedure is employed with the following modifications necessitated by the extreme instability of this compound. The low-temperature chromatography column is cooled by refluxing dimethyl ether (bp −23°). The solvent ether is removed by bulb-to-bulb distillation on a vacuum line at −25°. This yellow oil is only stable for about 5 hr when stored in the dark at −20°: nmr ($CDCl_3$) $\delta$ 1.37 (6 H, s), 4.38–5.85 (3 H, m), 6.73 (2 H, m), 7.30 (3 H, m); visible (octane) $\lambda_{max}$ 415 nm.

**Product Studies.** Sample tubes were prepared using 0.15 *M* *trans*-**6** in either cumene or benzene. The solutions were freeze–pump–thaw degassed and sealed off at 0.001 mm. The tubes were photolyzed to completion at 25° with 436-nm light, frozen, and cracked. Weighed amounts of either biphenyl or naphthalene standard were introduced and the products analyzed by vpc on an F&M Model 700 gas chromatograph. Injections were made onto matched 5% high efficiency Apiezon columns programmed from 65 to 175° at 7.5°/min.

**Racemization of *trans*-1 on Partial Photolysis.** *trans*-**1** ($[\alpha]_{452}$ +336°, $[\alpha]_D$ +82°, $\Delta\epsilon$ +0.34), 0.01 *M* in hexadecane, was photolyzed at 25° to 40% completion, and the remaining azo compound was recovered and purified by chromatography on alumina with 10:1 pentane–ether as eluent. Recovered **1** was shown to be uncontaminated by thin layer, ir, vis, and nmr, and had $[\alpha]_{452}$ +253°, $[\alpha]_D$ +61°, $\Delta\epsilon$ +0.25 indicating optical activity about 74% that of the starting azo compound. More dilute solutions gave the same result.

***cis*-6 Thermolysis.** Because of its stability, *cis*-**6**, could be weighed and dissolved in cold solvents with no decomposition. Solutions (0.02 *M*) were degassed and thermolyzed overnight at 25.00 ± 0.05°. Sample tubes were frozen and cracked, and the contents were quantitatively transferred to volumetric flasks which were then diluted to the mark. Visible spectra were taken and the percentage yield of trans calculated.

***cis*-1 Thermolysis.** Solutions (0.05 *M*) of *cis*-**1**, of known optical purity, were prepared and thermolyzed overnight at 25.00 ± 0.05°. The tubes were frozen and cracked, and the contents were chromatographed on alumina. *trans*-**1** was isolated, and heptane solutions of it were analyzed by visible and CD spectra.

**Quantum Yields.** Solutions (0.03 *M*) of **1** were frozen, pumped, thawed, and degassed in 2-cm matched Pyrex tubes. Photolyses were carried out on a merry-go-round apparatus using a medium-pressure Hg lamp filtered to transmit 436-nm light. Several tubes containing **1** in different solvents along with ferrioxolate actinometer tubes were photolyzed for a specified time period. The tubes containing **1** were allowed to stand 2 hours at 25° and diluted 1 to 5. **1** remaining was determined by uv analysis.

**Acknowledgments.** We gratefully acknowledge the expert synthetic assistance offered by Mr. Craig Rice and Mr. William Stewart.

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[39] This sample is identical with one in an earlier report: S. N. Ege and R. R. Sharp, *J. Chem. Soc. B*, 2014 (1971).

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# Photoreactions of Transition Metal Complexes. Ligand Reactivity as a Probe for Excited-State Characterization[1]

**Phoebe P. Zarnegar, C. R. Bock, and David G. Whitten*[2]**

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**Abstract:** An investigation of the photochemistry of a series of ruthenium(II)–4-stilbazole complexes is reported. The complexes under investigation, $[Ru(2,2'\text{-bipy})_2(\textit{trans}\text{-4-stilbazole})_2]^{2+}$ (**1**), $[Ru(2,2'\text{-bipy})_2(\textit{cis}\text{-4-stilbazole})_2]^{2+}$ (**2**), $[Ru(2,2'\text{-bipy})_2(\textit{trans}\text{-4-stilbazole})Cl]^{+}$ (**3**), and $[Ru(2,2'\text{-bipy})_2(\textit{cis}\text{-4-stilbazole})Cl]^{+}$ (**4**), undergo wavelength-dependent isomerization of the stilbazole ligand as their only important photoreaction under direct or sensitized irradiation in butyronitrile. A study of the details of the ligand cis → trans isomerization as a function of wavelength has demonstrated the reactivity of at least two different types of excited states that can serve as reactive intermediates. Irradiation into long wavelength transitions of these complexes generates charge-transfer excited states which appear best described as metal–oxidized-ligand radical anions. Activation with higher energy light produces states which appear very similar in behavior to the lowest excited states of the free ligand. In this case it appears that the wavelength effects are due to rapid reaction of the upper excited states instead of to slow radiationless processes.

Recent studies of the photochemistry of transition metal complexes and organometallic compounds have revealed a wide variety of interesting photoreactions including redox phenomena, ligand substitution, and isomerizations involving in various cases either or both complex and ligand.[3–6] In contrast to many organic systems, the inorganic complexes offer a rich array of possible excited states and to date characterization of the various excited states as to identity, lifetime, or reactivity has been limited. The common observation of wavelength effects here as compared with most organic molecules has raised questions as to whether radiationless processes are generally slower for

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[1] A preliminary account of a portion of this work has appeared: P. Zarnegar and D. G. Whitten, *J. Amer. Chem. Soc.*, **93**, 3776 (1971).

[2] Alfred P. Sloan Foundation Fellow.

[3] For a review, see V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

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[5] P. C. Ford, D. H. Stuermer, and C. P. McDonald, *J. Amer. Chem. Soc.*, **91**, 6209 (1969).

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the inorganic systems or if reactions from upper excited states are fast enough to compete with decay.[7–9]

One area which has been the focus of several recent investigations is the photochemistry of various ruthenium(II) complexes with nitrogen ligands such as $[Ru(NH_3)_5L]^{2+}$ and $[Ru(bipy)_2(L)_2]^{2+}$, where bipy = 2,2′-bipyridine and L = N-heteroaromatic ligand. Excited states of these complexes have been investigated both by spectroscopic techniques[8,10,11] and photochemical studies.[1,5,12,13] Absorption spectra of these complexes generally show two types of prominent transitions in the visible and near uv region: the longest wavelength transitions are usually assigned as metal → ligand (CTTL) $d,\pi^*$ transitions while those at somewhat shorter wavelengths can usually be identified as ligand-localized $\pi,\pi^*$ transitions.[14,15] Complexes such as $[Ru(bipy)_3]^{2+}$ and $[Ru(bipy)_2(py)_2]^{2+}$ are remarkably light stable[10] and show strong luminescence both in solution at room temperature as well as in a glass at low temperature.[8,11] This emission, which has been the subject of extensive investigation, has been assigned as phosphorescence ($\pi^* \rightarrow d$) from the lowest (CTTL) triplet of the complex.[8,11] For these complexes, as well as several other similar ruthenium complexes, there appears to be little wavelength effect on the emission probability. In contrast to the bipyridine complexes, the various pentaammine ruthenium(II) complexes with N-heteroaromatic compounds such as pyridine are mostly nonluminescent but they exhibit strongly wavelength dependent photoreactivity.[5,12] Various models have been suggested as explanations for these phenomena;[13] however, it is probably safe to conclude that at present the situation is not completely resolved.

In the present paper we report results of a photochemical investigation of some ruthenium(II) complexes of the type $[Ru(bipy)_2L_n]X_{2-n}$ where L is 4-stilbazole, a ligand containing an isomerizable olefinic bond, and X = $BF_4^-$ or $PF_6^-$, inert anions. These complexes undergo strongly wavelength-dependent cis–trans isomerization of the 4-stilbazole ligand as their only photoreaction and also exhibit wavelength-dependent luminescence. Through a careful study of the details of ligand cis–trans isomerization as a function of wavelength it has been possible to demonstrate the reactivity of at least two different types of excited states that can serve as reactive intermediates. Irradiation into long wavelength transitions of these complexes generates CTTL states which appear best described as metal oxidized–radical anions of the ligand. Activation with higher energy light produces states which appear very similar in behavior to the lowest excited states of the free ligand. Interestingly, in this case the wavelength effects appear to be due to rapid reaction of the upper excited states instead of to slow radiationless processes.

## Experimental Section

**Materials.** The bis(4-stilbazole)ruthenium(II) complexes, **1** and **2**, were prepared by refluxing excess *trans*- or *cis*-4-stilbazole with $Ru(bipy)_2Cl_2 \cdot 2H_2O$[16] in 50% aqueous methanol until the color of the solution had changed from deep purple to an orange-red (approximately 3 hr). An aqueous solution of $NaBF_4$ was added to the mixture and the methanol was then removed by distillation. The remaining aqueous solution was cooled for several hours during which orange crystals appeared. The crystals were collected by filtration and washed several times with hot benzene to remove the excess stilbazole. Purification was accomplished by repeated crystallizations from hot acetone–water mixtures. *Anal.* Calcd for $Ru(bipy)_2$(*trans*-4-stilbazole)$_2(BF_4)_2$ (**1**), $C_{46}H_{38}N_6B_2F_8Ru$: C, 58.19; H, 4.03; N, 8.85. Found: C, 57.97; H, 4.13; N, 8.93. Calcd for $Ru(bipy)_2$(*cis*-4-stilbazole)$_2(BF_4)_2$ (**2**), $C_{46}H_{38}N_6B_2F_8Ru$: C, 58.19; H, 4.03; N, 8.85. Found: C, 58.08; H, 4.05; N, 8.93.

The mono(4-stilbazole)ruthenium(II) complexes **3** and **4** were prepared from a ruthenium(II) nitrosyl chloride complex, $Ru(bipy)_2(NO)(Cl)(PF_6)_2$, which could be easily prepared from $Ru(bipy)_2Cl_2 \cdot 2H_2O$.[17] The nitrosyl chloride was treated with $KN_3$ by slow dropwise addition of a methanol solution of the azide to an acetone solution of the nitrosyl chloride. After the mixture was stirred for 15 min, the resultant solution was added dropwise to an acetone solution of excess *cis*- or *trans*-4-stilbazole at 35–50°. After the mixture was stirred for 45 min at this temperature, the solution was added dropwise to an excess of ether. The solid that precipitated was collected by filtration and washed several times with ether. Recrystallization from acetone–ether afforded pure complex. *Anal.* Calcd for $Ru(bipy)_2$(*trans*-4-stilbazole)$(Cl)(PF_6)$ (**3**), $C_{33}H_{27}N_5ClPF_6Ru$: C, 51.2; H, 3.49; N, 9.05. Found: C, 50.6; H, 3.53; N, 8.91. Calcd for $Ru(bipy)_2$(*cis*-4-stilbazole)$(Cl)(PF_6)$ (**4**), $C_{33}H_{27}N_5ClPF_6Ru$: C, 51.2; H, 3.49; N, 9.05. Found: C, 50.7; H, 3.35; N, 9.08.

Solvents used in the preparations were reagent grade, used as received. The solvent chosen for the majority for the irradiation experiments was *n*-butyronitrile. Commercial (Aldrich) *n*-butyronitrile was further purified by distillation first from $KMnO_4/Na_2CO_3$ and subsequently from $P_2O_5$. Absorption and emission spectra were measured in Spectrograde solvents, used as received.

**Photoisomerization Studies.** Isomerization quantum yields were obtained by irradiating samples degassed and sealed in Pyrex ampoules. Degassing and irradiation procedures have been previously described.[18] The concentration of complex in the *n*-butyronitrile solution was generally $5 \times 10^{-3}$ *M*. Due to the extreme light sensitivity of *cis*-4-stilbazole complexes **2** and **4** it was necessary to perform all operations in a darkened laboratory. In determining quantum yields, the isomerizations were carried to very low conversion (1–6%) to prevent the necessity of a back reaction correction; the determinations were done in triplicate.

Photostationary state determinations were carried out from both directions until analysis revealed no further change in the cis/trans ratio. Determinations were carried out several times on duplicate samples of each isomer.

Following irradiation, the tubes were opened and the solutions were treated with an excess of triphenylphosphine in the dark. The resulting solutions were refluxed for approximately 24 hr to free the stilbazole from the complex. Control experiments with unirradiated complex indicated that this procedure freed the stilbazole without causing measurable cis–trans isomerization. Vpc analysis of the control samples indicated that recovery of the stilbazole by this treatment was efficient to the extent of 90% or better. Analysis of the above refluxed solutions was by vpc on a Perkin-Elmer 881 chromatograph equipped with a flame-ionization detector. The column found most useful in separating the stilbazole isomers from each other and also from released 2,2′-bipyridine was 8 ft × $^1/_8$ in. of 2.5% SE-30 and 2.5% fluorosilicate on Chromosorb G.

**Spectra.** Absorption spectra were recorded on either a Unicam SP800B or a Cary Model 14 recording spectrophotometer. Emission spectra wre recorded on a Hitachi Model MPF-2A spectrophotofluorometer. The flash spectroscopic studies were carried out as previously described.[18,19]

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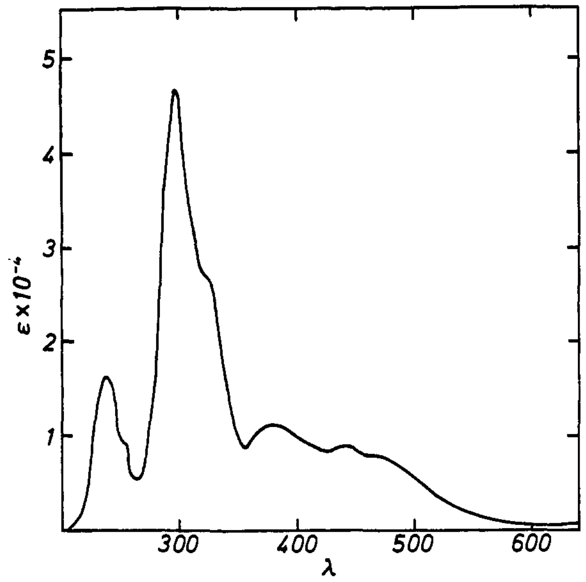

Figure 1. Absorption spectrum of bis(2,2′-bipyridine)bis(*trans*-4-stilbazole)ruthenium(II) fluoroborate in ethanol.

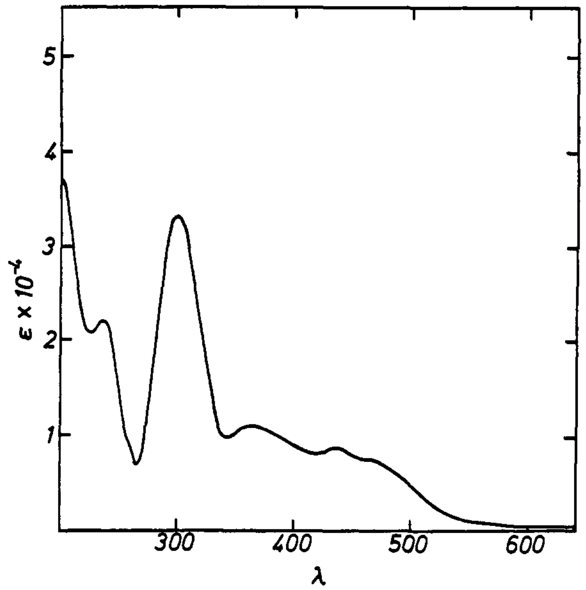

Figure 2. Absorption spectrum of bis(2,2′-bipyridine)bis(*cis*-4-stilbazole)ruthenium(II) fluoroborate in ethanol.

**Equilibration.** The thermodynamic cis–trans equilibrium of 4-stilbazole was determined by the iodine–nitrobenzene method.[20] Analysis of the cis/trans ratio was by vpc.

## Results

The 4-stilbazole complexes used in this study, **1**–**4** are thermally stable and undergo ligand exchange only under vigorous treatment with reagents such as triphenylphosphine or cyanide. Removal of the 4-stilbazole ligand without cis–trans isomerization was accomplished by heating the complexes in solutions containing concentrated triphenylphosphine in *n*-butyronitrile. That isomerization did not occur during synthesis, purification, or decomposition of the complexes was demonstrated by the recovery of only *cis*-4-stilbazole from unirradiated samples of **2** and **4** and of only *trans*-4-stilbazole from unirradiated **1** and **3**.

The stilbazole complexes **1**–**4** used in this study show absorption spectra similar to those of other ruthenium-(II)-2,2′-bipyridine complexes (Figures 1 and 2);[11,14,15] the addition of 4-stilbazole introduces new transitions in both the charge-transfer (340–500 nm) region and at shorter wavelengths. A subtraction spectrum (Figure 3) comparing the spectrum of **1** with that of $Ru(bipy)_2(py)_2^{2+}$ shows clearly the 4-stilbazole $\pi,\pi^*$ transitions, slightly reduced in intensity from that of the free ligand but at approximately the same wavelength, 315 nm, as well as the new CTTL bands at longer wavelengths. Compound **3** shows a similar spectrum while the *cis*-4-stilbazole complexes **2** and **4** show less prominent $\pi,\pi^*$ transitions near 295 nm, the transitions being similar again to those of the free ligand ($\lambda_{max}$ 285 nm).[21]

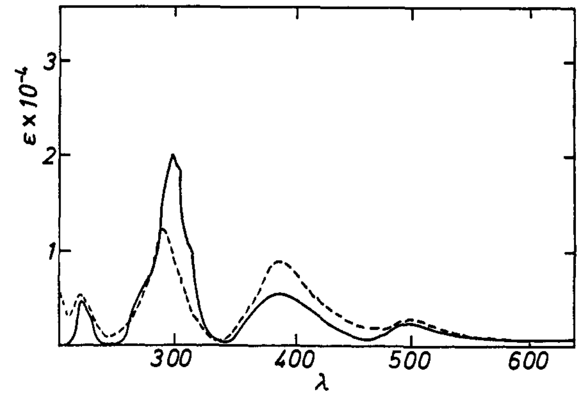

Figure 3. Subtraction spectra of bis(2,2′-bipyridine)bis(4-stilbazole)ruthenium(II) complexes minus spectrum of bis(2,2′-bipyridine)bis(pyridine)ruthenium(II): (—) *trans*-4-stilbazole complex; (- - - -) *cis*-4-stilbazole complex.

Irradiation of solutions of complexes **1**–**4** in several organic solvents[23] (*e.g.*, acetone, ethanol, and *n*-butyronitrile) leads to *cis–trans* isomerization of the stilbazole ligand as the only detectable reaction (Chart I). Irradiation of either **1** or **2** at any wavelength resulted in an isosbestic point at 267 nm; prolonged irradiation of **1** or **2** led to the same ligand photostationary state as determined from either absorption spectra or vpc analysis of released ligand. Irradiation led to interconversion of **3** and **4** as their only detectable photoreaction; in this case an isosbestic point at 265 nm was obtained (the isosbestic point for free 4-stilbazole cis–trans isomerization in *n*-butyronitrile is 267 nm). A striking feature of the initial irradiation studies of these complexes was the finding that irradiation with visible (436–550 nm) light (into the CTTL transitions) led to stationary states very rich in *trans*-4-stilbazole while irradiation into the $\pi,\pi^*$ transitions (313 nm) led to cis-rich stationary states (Table I). With degassed solutions it is possible to go through several cycles of cis–

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(21) The subtraction spectra here presented are quite similar to the spectra of *cis*- and *trans*-4-stilbazole complexes of pentaammineruthenium(II)$^{2+}$ where the only bands prominent above 250 nm are the stilbazole $\pi,\pi^*$ transitions, nearly unchanged from free ligand and a single charge transfer transition having $\lambda_{max}$ in the region 400–500 nm in each case.[22]

(22) C. R. Bock, unpublished results.

(23) *n*-Butyronitrile proved to be the solvent of choice for these studies owing to the high solubility of the complexes in the nitrile and also to its transparency in the uv.

**Chart I**

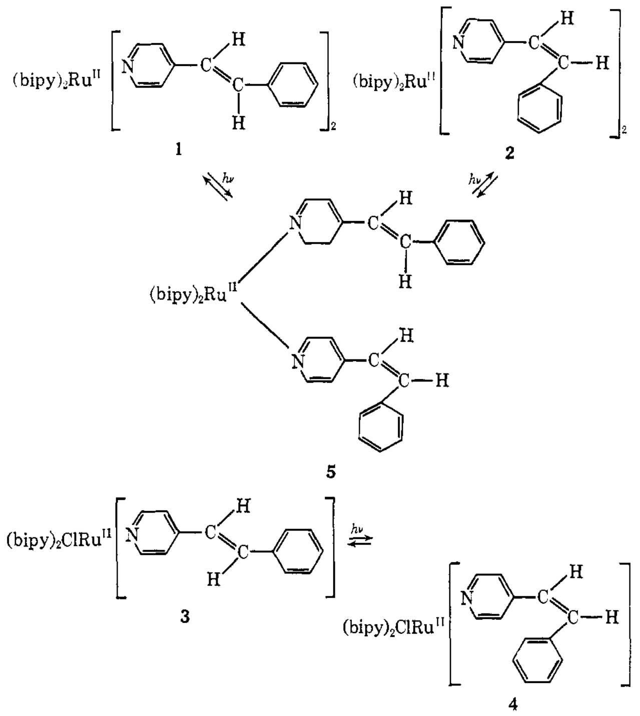

**Table I.** Photostationary States for Direct Irradiation of Ruthenium(II)-4-Stilbazole Complexes[a]

| Wavelength, nm | % trans isomer in photostationary state: Complexes **1** and **2** | % trans isomer in photostationary state: Complexes **3** and **4** |
|---|---|---|
| 313 | 35 ± 2.3 | 23.6 ± 1.1 |
| 366 | 88 ± 0.3 | |
| 436 | 85 ± 1.5 | 98.6 ± 0.9 |
| 570 | 88 ± 2.3 | |

[a] Butyronitrile solution, $T = 25°$.

trans ligand isomerization with only minor amounts of by-product formation or decomposition.

Measured and calculated initial quantum yields for isomerization of the 4-stilbazole ligand in **1**–**4** are listed in Table II. The calculated values were obtained from the stationary state relationship

**Table II.** Measured and Calculated Quantum Yields for Direct Isomerization of Ruthenium(II)-4-Stilbazole Complexes[a]

| Wavelength, nm | **1**, $\Phi_{t-c}$ | **2**, $\Phi_{c-t}$ | **3**, $\Phi_{t-c}$ | **4**, $\Phi_{c-t}$ |
|---|---|---|---|---|
| 313 | 0.15 | 0.156[a,b] | 0.092 | 0.123[a,b] |
| 366 | 0.05 | 0.15 | | |
| 436 | 0.05[a,b] | 0.51 | 0.035[a,b] | 0.665 |

[a] Butyronitrile solutions, $T = 25°$. [b] Calculated from the stationary state.

$$\Phi_{t-c}/\Phi_{c-t} = (c/t)_{pss}(\epsilon_c/\epsilon_t)$$

for cases where strong product absorption or the stationary state composition precluded direct measurement of the quantum yields. Although isomerization was the only detectable reaction in each instance, at no wavelengths do the quantum yields sums for **1** and **2** or for **3** and **4** equal unity. Interestingly, the highest quantum yields in each case were for the cis to trans process initiated by activation of the CTTL transitions.

Activation of **1** and **2** *via* photosensitization with Michler's ketone (4,4'-bis(dimethylamino)benzophenone, $E_t = 61$ kcal/mol),[24] zinc etioporphyrin I ($E_t = 41$ kcal/mol),[25] and etioporphyrin I (40 kcal/mol)[25] led also to cis-trans isomerization of the 4-stilbazole as the only detectable reaction. Stationary states and quantum yields are listed in Table III. Quantum yields for the sensitized reaction are very low both for zinc porphyrin and also for the higher triplet energy ketone even though the experiments were carried out with sensitizers having nearly quantitative intersystem crossing efficiencies[24,26] and under conditions where quantitative capture of sensitizer triplets by **1** and **2** occurs. The intense absorption of **1**–**4** over such a wide range of wavelengths severely limited the choice of sensitizers due to the risk of singlet sensitization. The porphyrins appeared to be particularly convenient sensitizers since their fluorescence was unquenched by the complexes while their triplets were efficiently quenched; a flash-spectroscopic investigation yielded for **1**, $k_q = 1.8 \times 10^9$, and for **2**, $k_q = 2.4 \times 10^9$ l. mol$^{-1}$ sec$^{-1}$ with the zinc etioporphyrin I triplet. From emission studies (*vide infra*) it can be estimated that the phosphorescent state of **1** lies at ~53 kcal/mol, an energy substantially higher than that of zinc etioprophyrin I. However, the quenching constant listed above is less than an order of magnitude below the diffusion-controlled value for a "classical" triplet energy transfer process; this indicates a maximum endothermicity of ~1 kcal/mol.[27] Consequently, it is necessary to use caution in interpreting the sensitization experiments, particularly those involving the porphyrin as sensitizer.

**Table III.** Sensitized Isomerization of Ruthenium(II)-4-Stilbazole Complexes[a]

| Sensitizer | $E_T$, kcal/mol | % trans photostationary state | Quantum yields |
|---|---|---|---|
| Michler's ketone | 61 | 65 ± 2.1 | $\Phi_{t-c} = 0.03$<br>$\Phi_{c-t} = 0.04$ |
| Zinc etioporphyrin I | 41 | 96 ± 2.9 | $\Phi_{t-c} = 0.001$<br>$\Phi_{c-t} = 0.02$ |
| Etioporphyrin I | 40 | 93 ± 1.0 | |

[a] Butyronitrile solution, $T = 25°$; starting isomers **1** and **2**.

Contrary to our preliminary findings (which employed a phototube having somewhat lower sensitivity in the visible region), we find upon reinvestigation that both **1** and **2** show weak emission in solution and somewhat stronger emission in a methanol-ethanol glass at 77°K. The emission occurs to the red of the longest wavelength CTTL bands with $\lambda_{max}$ 615 nm for both **1** and **2**. The quantum yield is apparently quite wavelength dependent; the strongest emission occurs upon activation in the CTTL band while activation into the $^1\pi,\pi^*$ bands produces only very weak emission. The efficiency for **1** upon activation at 450 nm is ~$10^{-3}$.

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## Discussion

Probably the most striking result of these investigations is the finding of such pronounced wavelength effects on both isomerization quantum efficiencies and photostationary states. For example, the observation that isomerization efficiencies for cis isomers **2** and **4** *decrease* sharply upon changing the irradiating wavelength from 436 to 313 nm indicates that most of the excited states formed at the latter wavelength must decay by paths that avoid the lowest excited singlet state. *Maximum* efficiencies of forming the lower (436 nm) state (calculated by comparing the isomerization yields) are 30% for **2** and 20% for **4**. To develop a clearer picture of the wavelength effects it is useful to consider possible mechanistic pathways.

Both the mono(4-stilbazole) complexes **3** and **4** and the bis(4-stilbazole) complexes **1** and **2** show similar behavior. For the latter complexes it is almost certain that isomerization proceeds *via* a *cis*-4-stilbazole–*trans*-4-stilbazole complex (**5**) (Chart I). However, in irradiation of either **1** or **2** an isosbestic point is obtained at 267 nm, the only point where the spectra intersect. This observation, as well as the spectral similarities of bound and unbound 4-stilbazole, suggests that in **1** and **2** the two 4-stilbazoles behave largely independent of one another. If we make this assumption for **1** and **2** and ignore the intermediate complex **5**, then a common mechanism may be drawn for both sets of complexes. The simplest mechanism that can be written consistent with the results would involve cis–trans isomerization proceeding through a common excited intermediate formed by decay of the initially formed excited states of the complexes such as is outlined in eq 1–7, where c = cis complex (**2** or **4**) and

$$\mathrm{c} \xrightarrow{h\nu} \mathrm{c}^{1*} \tag{1}$$

$$\mathrm{t} \xrightarrow{h\nu} \mathrm{t}^{1*} \tag{2}$$

$$\mathrm{c}^{1*} \xrightarrow{k_1} \mathrm{I}^* \tag{3}$$

$$\mathrm{t}^{1*} \xrightarrow{k_1} \mathrm{I}^* \tag{4}$$

$$\mathrm{I}^* \longrightarrow \alpha(\mathrm{c}) + (1 - \alpha)(\mathrm{t}) \tag{5}$$

$$\mathrm{c}^{1*} \xrightarrow{k_3} \mathrm{c} \tag{6}$$

$$\mathrm{t}^{1*} \xrightarrow{k_4} \mathrm{t} \tag{7}$$

t = trans complex (**1** or **3**) and I* = a common intermediate. The efficiency of forming I* from the initially formed excited states is given by $n = k_1/(k_1 + k_3)$ and $m = k_2/(k_2 + k_4)$ such that the initial quantum yields are given in eq 8 and 9. The stationary state relationship at any wavelength is given by eq 10. A "decay

$$\Phi_{\mathrm{c-t}} = n(1 - \alpha) \tag{8}$$

$$\Phi_{\mathrm{t-c}} = m\alpha \tag{9}$$

$$\left(\frac{\mathrm{c}}{\mathrm{t}}\right)_{\mathrm{pss}} = \frac{(\alpha)}{(1 - \alpha)}\frac{(m)}{(n)}\frac{(\epsilon_{\mathrm{t}})}{(\epsilon_{\mathrm{c}})} = \frac{(\Phi_{\mathrm{t-c}})(\epsilon_{\mathrm{t}})}{(\Phi_{\mathrm{c-t}})(\epsilon_{\mathrm{c}})} \tag{10}$$

factor," $D_{\mathrm{c/t}}$, can be obtained by correcting the photostationary state value for differences in extinction coefficient (eq 11). Values of $D_{\mathrm{c/t}}$ at various wavelengths are listed in Table IV.

$$D_{\mathrm{c/t}} = \left(\frac{\mathrm{c}}{\mathrm{t}}\right)_{\mathrm{pss}}\frac{(\epsilon_{\mathrm{c}})}{(\epsilon_{\mathrm{t}})} = \frac{(\alpha)}{(1 - \alpha)}\frac{(m)}{(n)} = \frac{\Phi_{\mathrm{t-c}}}{\Phi_{\mathrm{c-t}}} \tag{11}$$

**Table IV.** Calculated Values of the "Decay Factor," $D_{\mathrm{c/t}}$, for Ruthenium(II)-4-Stilbazole Complexes

| | $D_{\mathrm{c/t}}$ | |
|---|---|---|
| Wavelength, nm | **1–2** | **3–4** |
| 313 | 0.96 | 0.75 |
| 366 | 0.14 | |
| 436 | 0.10 | 0.006 |
| 546 | 0.004 | |

The values of $D_{\mathrm{c/t}}$ show a pronounced wavelength dependence; for both pairs of complexes a sharp decrease in $D_{\mathrm{c/t}}$ occurs as the irradiating wavelength is shifted from the $^1\pi,\pi^*$ transition to the charge-transfer band. Thus while the mechanism outlined above is adequate for any single wavelength, it is clear that as the wavelength of irradiation is changed there occurs either a change in the reactive state I* or else a change in the relative efficiencies of forming I* from $\mathrm{c}^{1*}$ or $\mathrm{t}^{1*}$ or both.

To develop a clearer picture of the mechanistic possibilities it is useful to consider two limiting cases. A first possibility (case A) could be that a single intermediate I* with a constant decay ratio, $\alpha/(1 - \alpha)$, is responsible for the isomerization at all wavelengths for each set of complexes. The wavelength effect would then be due to a changing ratio of $m/n$; values for $m/n$ assuming an olefin excited state with $\alpha/(1 - \alpha) \sim 1$ then decrease from near unity to ~0.005 at long wavelengths for both sets of complexes. Since values of $\Phi_{\mathrm{c-t}}$ reach (actually exceed) 0.5, the value of $m$ would have to increase from ~0.2 to unity at long wavelengths while the efficiency of populating I* from the excited state initially formed from trans[5] complexes **1** and **3** would have to simultaneously decrease from 0.2 to 0.3 at 313 nm to a value of only ~0.005 at long wavelengths (546 nm).

A second limiting possibility (case B) is that the decay ratio varies due to the participation of different intermediates while the values of $n$ and $m$, or at least the $m/n$ ratios, remain constant. If $m/n$ has a value of unity for both complexes at all wavelengths, then values for the decay ratio range from near unity when excitation is into the olefin $^1\pi,\pi^*$ transitions and 0.005 where the purely charge-transfer transitions are activated.

It would appear reasonable that the true situation should be somewhere intermediate between the extremes of the two limiting cases. As far as case A is concerned, it appears unlikely that the total effect can be ascribed simply to variations in $n$ and $m$. Some variation of $n$ and $m$ with wavelength would certainly be expected, particularly in view of the variety of overlapping electronic transitions in the spectra of the complexes which include transitions largely associated with the bipyridine ligand (both the $^1\pi,\pi^*$ transition with $\lambda_{\mathrm{max}}$ near 293 nm and perhaps more important the $^1\mathrm{d},\pi^*$ transitions in the range 430–440 nm). On the other hand, it appears unlikely that complications from excited states involving the remainder of the complex could cause the systematic variation of $D$ that is actually observed.[28]

The possibility that the observed results can be ascribed largely to the participation of different inter-

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(28) For example, since both sets 1–2 and 3–4 have approximately the same band onset for cis and trans isomers it appears unlikely that activated energy transfer to a common intermediate should be substantially faster from lowest "spectroscopic" singlets 2 and 4 compared to 1 and 3.

mediates appears reasonable, particularly upon consideration of some additional data regarding the cis–trans isomerization of 4-stilbazole. As previously mentioned, typical decay ratios ($\alpha/(1 - \alpha)$) for common (presumably twisted) excited singlet and triplet states of olefins are near unity;[29] the value for the 4-stilbazole singlet obtained from direct irradiation is 1.36[30] while the triplet value is 1.01.[31] In contrast, when 1,2-diarylethylenes such as the stilbazoles or stilbene are converted to their radical anions or otherwise equilibrated with reagents such as iodine, the mixture that results is nearly all trans;[20,32,33] for 4-stilbazole the thermodynamic cis–trans ratio determined by iodine equilibration in nitrobenzene is 0.006. Thus, a process involving a twisted olefin excited state of the stilbazole as the isomerization intermediate would be expected to have a decay ratio near unity, while a process with a radical anion of the stilbazole (or other radical adduct) as isomerization intermediate would be expected to yield a decay ratio of $\sim$0.006. In fact, the limiting values for both sets (0.96 and 0.004 for **1–2** and 0.75 and 0.006 for **3–4**) are remarkably close to these values. The most reasonable interpretation of the present results is thus that irradiation into the long wavelength bands of complexes **1–4** produces a CTTL excited state which behaves similar to a radical anion of the olefin–ligand and results in preferential cis-to-trans isomerization. Irradiation at shorter wavelengths produces predominantly excited states of the olefin–ligand which decay with nearly equal probability to cis and trans ground states. The fact that values of $D_{c/t}$ are somewhat lower than the measured excited state decay ratios for 4-stilbazole possibly indicates the extent of leakage that occurs *via* lower energy CTTL states.[34–36]

Two major points of interest regarding ligand isomerization in these complexes concern the participation of olefin triplet states and the lifetime of the reactive upper excited states. Regarding the former, the limited sensitization experiments appear to indicate that isomerization from triplet states of complexes **1** and **2** may be relatively inefficient. The experiments with Michler's ketone as sensitizer were done under conditions where total quenching of sensitizer triplets occurs and with a sensitizer energetic enough to form "spectroscopic" triplet states of the olefin. Nevertheless, isomerization yields with Michler's ketone are very low. Quenching of sensitizer triplets does not, of course, guarantee formation of acceptor triplets so the exact efficiency of isomerization from complex triplets remains uncertain. However, if the isomerization efficiencies measured using Michler's ketone as sensitizer in fact indicate low isomerization efficiencies from the triplet state, an attractive possibility for explaining the lower than unit sum for $\Phi_{c-t} + \Phi_{t-c}$ in the direct isomerization could be ruthenium-catalyzed intersystem crossing to an unreactive triplet. We have previously found that direct irradiation of both 4-stilbazole as well as its quaternary salt results in little or no formation of triplet states;[37] however, external heavy atoms and oxygen can induce efficient intersystem crossing in the quaternary salt[38] and thus it is reasonable that the internal ruthenium could produce a similar effect.

Regarding the lifetime of the upper excited states of the complex, the fluorescent rate constant for the $^1\pi,\pi^*$ transition of bound *trans*-4-stilbazole should be near $5 \times 10^8$ sec$^{-1}$.[37] An upper limit to the quantum yield for this fluorescence (undetected) for **1** would be $\Phi_f \approx 10^{-4}$. The latter value than indicates a lifetime for the upper excited state of $\leq 2 \times 10^{-13}$ sec; if we assume a leakage to the state formed by irradiation at 436 nm of 10% (*vide supra*) we get $k_{ic} \approx 5 \times 10^{12}$ sec$^{-1}$. Such a value, which must be regarded as tentative due to the numerous uncertainties involved, is reasonably close to those observed in other molecules where small separations occur between upper excited states.[39,40] Therefore, it would appear in this case that the striking wavelength effects are due to relatively fast reaction from the upper excited state and not to an intrinsically slow radiationless process.

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[34] The differences between $D_{c/t}$ and the stilbazole decay ratios could also be due to other factors; for example *n*/*m* values different from unity.

[35] Whether this represents a radiationless process prior to formation of the twisted olefin state or decay to the CTTL state from the twisted state is uncertain; the former possibility appears to be more reasonable.

[36] Calculated "leakages" depend heavily on the assumed decay ratio; assuming ($\alpha/(1 - \alpha)$) = 1 a value of 4% leakage is obtained, while from ($\alpha/(1 - \alpha)$ = 1.3 a value of 26% is obtained.

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