Photochemistry of Ruthenium Complexes. Ligand Isomerization *via* Orbitally Different Excited States

Sir:

Recently there has been considerable interest in the role, lifetime, and nature of metastable excited states in the photochemistry of transition metal complexes.[1-4] Organic molecules having more than one low-lying excited state show wavelength effects in their solution photochemistry only in exceptional cases.[5,6] Transition-metal complex photochemistry is frequently wavelength dependent; however, most complexes showing this dependence undergo bond breakage which frequently can be related to the transition involved in initial excitation.[1-3,7] There has been concern over whether caged radical pairs or excited states are responsible for these photodissociations.[1-3,8] Although excitation wavelength independent emission from various types of excited states (ligand, metal, and mixed) has been observed from several complexes,[9-11] most photochemically active transition metal complexes with unfilled orbitals neither emit nor survive long enough in solution to be detected by flash spectroscopy or by energy transfer to low-energy acceptors. In the present paper we report an investigation of the photochemistry of two ruthenium complexes of 4-stilbazole: bis(2,2′-bipyridine)–bis(*trans*-4-stilbazole)ruthenium(II) fluoroborate (**1**) and bis(2,2′-bipyridine)–bis(*cis*-4-stilbazole)-ruthenium(II) fluoroborate (**2**). These complexes do not photodissociate but undergo cis–trans isomerization of the ligand as their only photoreaction. By using isomerization of the 4-stilbazole ligand in direct and sensitized reactions as a probe, we demonstrate the probable reactivity of excited states of different orbital origin. Interestingly we find that interconversion of the different excited states is evidently slow compared with isomerization of the ligand and nonradiative decay of the excited complex.

Complexes **1** and **2** were prepared by refluxing Ru-(2,2′-bipyridine)$_2$Cl$_2$·2H$_2$O[12] with *trans*- and *cis*-4-stilbazole, respectively, in 50% methanol. Addition of NaBF$_4$ with subsequent removal of methanol precipitated the crystalline complexes.[13] Complexes **1** and **2** are stable at room temperature in the crystalline state and in solution; they are also substitution inert. The ruthenium complexes can be decomposed to liberate free 4-stilbazole without cis–trans isomerization by refluxing with excess triphenylphosphine. Analysis for cis–trans isomerization was by vpc.[14]

The absorption spectra of the two ruthenium complexes show transitions typical of related ruthenium compounds.[10,15] The lower energy transitions (340–500 nm) are identified as charge transfer–ligand (CTTL) d → π* transitions.[16] The 4-stilbazole π → π* transitions have $\lambda_{\max}$ *ca.* 315 nm, slightly reduced in intensity, near the wavelength where uncomplexed olefin absorbs.[14] The bipyridine π → π* band has $\lambda_{\max}$ 293 nm. No luminescence was detected from room temperature solutions of **1** and **2** in butyronitrile at wavelengths where 4-stilbazole fluoresces[14] or where tris-(2,2′-bipyridine)ruthenium(II) chloride emits.[17] No emission could be detected from **1** or **2** in EPA glass at 77°K under conditions where fairly strong luminescence from tris(2,2-bipyridine)ruthenium(II) chloride and other ruthenium complexes is observed.[10]

Direct irradiation of the ruthenium complexes in purified butyronitrile led to cis–trans isomerization of the 4-stilbazole ligand as the only detectable reaction.[18-22] Analysis of irradiated solutions indicated a pronounced wavelength effect; irradiation of **2** with visible light caused efficient and nearly complete conversion to **1**. In contrast, irradiation of **1** in the ultraviolet (313 nm) produced efficient isomerization in the opposite direction. Stationary states and quantum yields obtained at various wavelengths are listed in Table I. To correct the photostationary states for spectral differences in **1** and **2** at various wavelengths, we introduce the cis–trans decay factor, $D_{c/t} = ([\text{cis}]/[\text{trans}])_{\text{pss}}(\epsilon_{\text{cis}}/\epsilon_{\text{trans}})$.

Table I. Direct Isomerization of 4-Stilbazole in Ruthenium Complexes **1** and **2**

λ, nm	Photostationary state, % trans[a]	Quantum yields	Decay factor[b]
313	35 ± 2.3	$\phi_{t\to c} = 0.15$	0.96
366	80 ± 0.3	$\left\{\begin{array}{l}\phi_{t\to c} = 0.05\\ \phi_{c\to t} = 0.15\end{array}\right.$	0.14
405, 436	85 ± 1.5	$\phi_{c\to t} = 0.51$	0.10
546	88 ± 2.3		0.004

[a] Measured from both directions. [b] See text.

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(16) Comparison of the spectra of 1 and 2 with those of other ruthenium complexes indicates that the d → π* (4-stilbazole) transitions have $\lambda_{\max}$ at 375 and 470 nm for 1 and 370 and 460 nm for 2.

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(22) An isosbestic point is observed at 267 nm, the only point where the spectra of 1 and 2 intersect. However, the isomerization most probably proceeds *via* a *cis*-4-stilbazole–*trans*-4-stilbazole complex in every case. The observation of the isosbestic point (as well as spectral similarities of bound and unbound stilbazoles) is in accord with the implicit assumption that the two 4-stilbazoles behave independently of one another.

Table II. Sensitized Ligand Isomerization in **1** and **2**[a]

Sensitizer	E_T, kcal/mol	ϕ_{isc}	Photostationary state, % trans	Quantum yields
Michler's ketone	61[b]	1.01[b]	65 ± 2.1	$\phi_{t \to c} = 0.03$ $\phi_{c \to t} = 0.04$
Zinc etioporphyrin **I**	41	0.9[c]	96 ± 2.9	$\phi_{t \to c} = 0.001$ $\phi_{c \to t} = 0.02$
Etioporphyrin I	40		93 ± 1.0	

[a] Butyronitrile solution, $T = 25°$. [b] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 131. [c] B. Dzhagarov, *Opt. Spektrosk.*, **28,** 66 (1970).

Photosensitization experiments with **1** and **2** as acceptors and various donors (Table II) also led to cis–trans isomerization of the 4-stilbazole as the only detectable reaction. The intense absorption of **1** and **2** at most wavelengths in the uv and visible limited the number of sensitizers that could be used without risk of singlet sensitization.[23,24] The porphyrins proved to be good sensitizers since their fluorescence was unquenched by **1** and **2** while their triplets were quenched (measured by flash spectroscopy) at rates ($k_1 = 1.8 \times 10^9$ and $k_2 = 2.4 \times 10^9$ l. mol^{-1} sec^{-1}) close to diffusion controlled. Although acceptor concentrations were high enough (1.5×10^{-3} M) to ensure that all sensitizer triplets were quenched for each of the sensitizers listed in Table II, quantum yields for isomerization were very low. Since triplets of **1** and **2** are not spectroscopically detectable, it is uncertain whether quenching is accompanied by efficient energy transfer.

The large variation in $D_{c/t}$ and the quantum yields with wavelengths on direct irradiation suggests that two or more isomerizable exited states are involved in the photochemistry of **1** and **2**.[25] Irradiation at 313 nm, where initial excitation is predominantly into the 4-stilbazole π–π^* transition, yields $D_{c/t} = 0.96$, a value fairly close to the value of 1.36 obtained in the direct isomerization of uncomplexed 4-stilbazole.[26] As irradiation is shifted to longer wavelengths where excitation is predominantly into the CTTL bands, $D_{c/t}$ decreases. The value $D_{c/t} = 0.004$ at 546 nm, where no direct excitation of 4-stilbazole $\pi \to \pi^*$ transitions occurs, is very close to the thermodynamic cis–trans ratio of 0.006 determined by iodine–nitrobenzene equilibration.

We suggest that isomerization initiated by irradiation of **1** and **2** at 313 nm occurs *via* the $^1\pi$–π^* state of the bound 4-stilbazole and that the isomerization initiated by longer wavelength irradiation arises from a lower energy charge-transfer state. The preferential cis → trans isomerization is reasonable for a charge-transfer state in which an electron has been transferred to an antibonding orbital of the 4-stilbazole.[27,28] It is most interesting to find so little leakage between the different excited state pathways.[29,30] This cannot be due exclusively to rapid formation of a twisted olefin state upon activation of the 4-stilbazole transitions since the quantum yields do not sum to unity. Nonradiative pathways that avoid the lower energy ^{1}CTTL* state are evidently followed. It remains to be determined whether this is a consequence of unusually short excited state lifetimes for the complex or of relatively slow rates for internal conversion between the $^1\pi$–π^* and ^{1}CTTL* states. Further studies on the reactivity of related complexes are in progress.

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(29) The situation regarding similar possibilities in the sensitized reaction is more complicated; discussion is deferred to the full paper.

(30) Interestingly, the present results contrast to those obtained in a study of a (*trans*-stilbenecarboxylato)cobalt(III)[4a] where extensive energy transfer was observed to dominate olefin isomerization upon irradiation of the stilbene π–π^* transitions.

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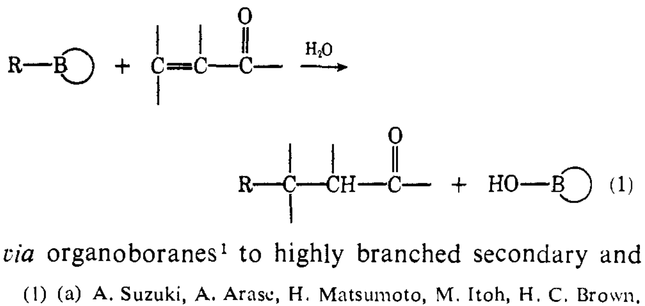
The Facile Reaction of *B*-Alkylboracyclanes with α,β-Unsaturated Carbonyl Derivatives. Extension of the 1,4-Addition Reaction *via* Organoboranes to Highly Branched Secondary and Tertiary Alkyl Groups

Sir:

Certain readily synthesized *B*-alkylboracyclanes undergo a facile reaction with methyl vinyl ketone and similar α,β-unsaturated carbonyl derivatives to transfer the *B*-alkyl group from boron to carbon, especially readily when the *B*-alkyl group is secondary or tertiary (eq 1). This extension of the 1,4-addition reaction



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via organoboranes[1] to highly branched secondary and

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