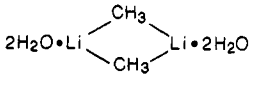
Table I. $^1H^a$ and $^{13}C^b$ NMR Spectra [$\delta$ ($Me_4Si$), ppm] of $(II)_2$

| temp, °C | $H_{a'}$ | $H_a$ | OMe | $H_b$ | $H_{b'}$ | $H_c$ | $C1(H_aH_{a'})$ | OMe | $C2(H_bH_{b'})$ | $C3(H_c)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 23 | 3.671<br>$m^c$ | 3.445<br>$m^c$ | 3.338<br>s | 2.202<br>$m^c$ | 1.860<br>$m^c$ | −1.055<br>$tt^c$ | 78.3<br>t, 139 Hz | 58.3<br>q, 139 Hz | 41.4<br>t, 118 Hz | 24.6<br>br s |
| −90 | 3.67<br>br m | 3.44<br>br m | 3.358 s<br>3.318 s<br>(1:1) | 2.22 br m<br>2.19 br m<br>(1:1) | 1.87 br m<br>1.84 br m<br>(1:1) | −1.055<br>$tt^c$ | | | | |
| −100 | | | | | | | 77.6 t<br>77.2 t<br>(1:1) | 57.4 q | 39.8 t | $d$ |

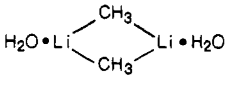
[a] In $n$-$C_5D_{12}$. [b] In $C_6D_6$ (23 °C) and cyclopentane (−100 °C). [c] $J$(Hz): a′a, 7.8; a′b, 11.4; a′b′, 2.7; ab, 4.2; ab′, 3.2; bb′, 13.8; bc, 12.3; b′c, 5.3. [d] Coincides with signal of cyclopentane ($\delta$ 25.3).

in rate-determining steps such as III → IX (→ V → IX′ → III′) or III → X (→ III′) is partially compensated by stronger bonding of the chelate moieties that remain attached to the tricoordinated lithium atom(s) in IX (X).[11]

Model MNDO calculations on XI and XII



XI



XII

indicate that 80% of the coordination energy of XI is retained in XII![12] Greater steric accessibility and neutralization of negative charge on carbon by two lithium cations (instead of three, in the case of tetramers) have been adduced as possible causes for the higher reactivity of organolithium dimers vs. tetramers.[2a] Greater ease of displacement of a solvating Lewis base by the reactant in the precoordination step of organolithium reactions[13] is now offered as an additional reason. The broadening in the proton spectrum at the lower temperature limit of −110 °C is tentatively ascribed to the loss of conformational mobility of the chelate rings. At 71 °C inversion of C3 ($H_c$ quintet) occurs with $\Delta G^{\ddagger} > 16$ kcal/mol (separate signals for $H_b$ and $H_{b'}$).

The effect on reactivity of lowering the degree of aggregation from 4 to 2 and doubling the number of solvating ether molecules was assessed for secondary alkyllithiums by comparing the reactivities of $(II)_2$ and tetrameric 3-lithio-1-methoxybutane $(XIII)_4$.[6a] In competition experiments involving benzaldehyde and a mixture in pentane of $(II)_2$ and $(XIII)_4$ (each in eightfold molar excess and each showing its own typical $^1H$ and $^7Li$ NMR signals), the ratio of the secondary alcohols formed provided values of $k_{(II)_2}{:}k_{(XIII)_4}$ of 3.0 (23 °C) and 7.5 [−17 °C, $\Delta\Delta H^{\ddagger} = 3.4$ kcal/mol, $\Delta\Delta S^{\ddagger} = 9.5$ cal/(mol K)]. In separate experiments at 26 °C terminated after 77 h by quenching with $ClSnMe_3$, $(II)_2$ and $(XIII)_4$ (0.224 mmol) dissolved in a mixture of 9.7 mL of pentane and 0.6 mL of toluene (5.6 mmol) gave $\alpha$-(trimethylstannyl)toluene in 11.4% and 3.9% yield, respectively. Relative reactivity data are available for two other alkyllithium dimers: at 50 °C, yields of benzyllithium from menthyllithium (dimer) and cyclohexyllithium (tetramer and/or hexamer) dissolved in toluene were 35% and 6.2%, respectively.[14] At −85 °C in THF, I reacts with benzaldehyde about 10 times faster than the tetramer.[15] Though the results of the present and the former studies are strikingly similar we refrain from generalizing, since the differences between the systems compared are still considerable.

**Acknowledgment.** We thank G. Schat for the association measurements.

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(11) Since no Li–O coordinative bond has to be broken, internal rotation in $(n\text{-}BuLi)_2$ (see ref 3) is presumed to be even faster than the processes operating on $(II)_2$.

(12) See also ref 1a, p 364. According to MNDO, synchronous exchange of the two Lewis base ligands at the same lithium atom is less favorable than processes leading to IX or X.

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## Slow Triplet Energy Transfer to Lower Excited States in Ruthenium(II) Acylpyridine Complexes

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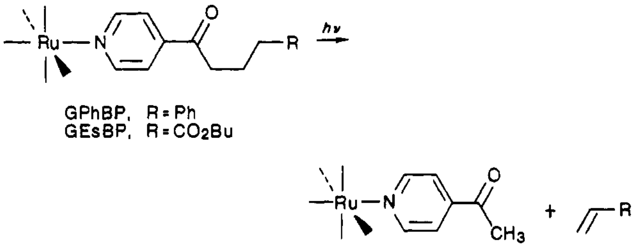
*Received July 17, 1986*

A few years ago we reported that locally excited acylpyridine (AP) triplets in $Ru^{II}(NH_3)_5AP$ complexes undergo relatively slow internal conversion (IL → MLCT) to the lower lying metal-to-ligand charge-transfer states.[1] At that time, we could merely place a maximum value of $10^8$ $s^{-1}$ on the rate constant $k_{ic}$ for such internal conversion. We now can report the actual value more precisely. We also find that internal quenching of triplet acylpyridines in $Ru^{II}(bpy)_2(AP)_2$ complexes by triplet energy transfer from acylpyridine to bipyridine is unexpectedly slow, unique behavior for two organic chromophores held so close together.



We have studied the reactivity of two 4-acylpyridines: $p$-($\gamma$-phenylbutyryl)pyridine (GPhBP) and $p$-($\gamma$-carbobutoxybutyryl)pyridine (GEsBP). As Table I shows, these two ketones undergo Norrish type II photoelimination[2] in identical quantum efficiency in acetonitrile. Stern–Volmer quenching studies, with ethyl sorbate as quencher, indicate that triplet GEsBP is only 6% as reactive as triplet GPhBP, as anticipated from earlier studies.[3] Likewise, the two hydrochloride salts react with the same quantum efficiency as each other and exhibit the same ratio of triplet reactivities. As is now well understood,[4] the observation of identical quantum yields but much different triplet lifetimes indicates that the triplets undergo no reaction except $\gamma$-hydrogen abstraction ($k_r = 1/\tau$) and that quantum yields are determined solely by later biradical partitioning.

The $Ru(NH_3)_5(AP)(BF_4)_2$[1] and $Ru(bpy)_2(AP)_2(BF_4)_2$[5] complexes were prepared as described in the literature. Irradiation at 313 nm of 0.004–0.04 M acetonitrile solutions did not cause

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0002-7863/87/1509-2188$01.50/0

**Table I.** Photokinetic Parameters for Free and Complexed 4-Acylpyridines[a]

| system | $\epsilon_{313}$[b] | $\Phi_{II}$[c] | $\Phi_{corr}$[d] | $1/\tau$[e,f] | $k_r$[e] | $k_d$[e,g] |
|---|---|---|---|---|---|---|
| free GEsBP | 112 | 0.41 | 0.41 | 0.6 | 0.6 | |
| free GPhBP | 124 | 0.42 | 0.42 | 10.0 | 10.0 | |
| GEsBP–HCl | 82 | 0.10 | 0.10 | 3.2 | 3.2 | |
| GPhBP–HCl | 104 | 0.09 | 0.09 | 50 | 50 | |
| $Ru(NH_3)_5GEs$ | 430 | 0.005 | 0.027 | 1.5 | 0.7 | 0.8 |
| $Ru(NH_3)_5GPh$ | 430 | 0.014 | 0.056 | 15 | 14 | 0.8 |
| $Ru(bpy)_2(GEsBP)_2$ | 7900 | 0.0017 | 0.082 | 4.2 | 1.2 | 3.0 |
| $Ru(bpy)_2(GPhBP)_2$ | 7700 | 0.0072 | 0.27 | 30 | 27 | 3.0 |

[a] 0.01 M $CH_3CN$ solutions irradiated at 313 nm. [b] Molar extinction coefficient. [c] Quantum yield of styrene or butyl acrylate at ≤10% conversion, average of duplicate measurements. [d] Quantum yield corrected for fraction of light absorbed by acylpyridine. [e] Units of $10^8$ s$^{-1}$. [f] From Stern–Volmer slopes ($k_q\tau$) with ethyl sorbate quencher, average of duplicate measurements; $k_q = 1 \times 10^{10}$ M$^{-1}$ s$^{-1}$. [g] $k_d = 1/\tau - k_r$.

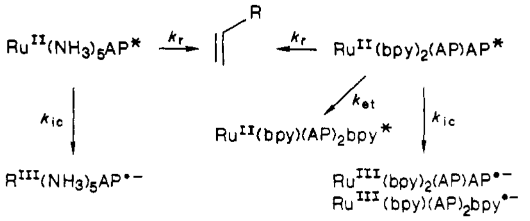
loss of GPhBP or GEsBP from the complexes[6] but did produce the styrene and butyl acrylate formed by type II elimination. Some, but not all, of the corresponding acetylpyridine could be released by treating the solutions with triphenylphosphine.[5] Table I lists the pertinent photokinetic information. The percentage of 313-nm radiation absorbed by the acylpyridine ligands was determined from the measured extinction coefficients of the free ligand hydrochloride and of the complex.

For both kinds of complex, type II quantum yields are lower for GEsBP than for GPhBP, unlike the situation for the uncomplexed ligands. Therefore the slow-reacting triplet GEsBP must be undergoing some form of decay competitive with hydrogen abstraction. Our earlier work[1] showed that complexed acylpyridines whose triplets are as reactive as that of GPhBP undergo no competitive triplet decay. Therefore the simple ratio of absorption-corrected quantum yields for GEsBP vs. GPhBP complexes should equal the fraction of complexed GEsBP that undergoes the type II reaction. The total rate of triplet decay, as determined from quenching studies, can thus be separated into values of $k_r$ and $k_d$. The fact that $k_r$ for complexed GEsBP is roughly 6% that for complexed GPhBP in both types of complexes, and midway between the $k_r$ values for free and protonated ligands, is strong confirmation of the accuracy of these rate constant determinations.

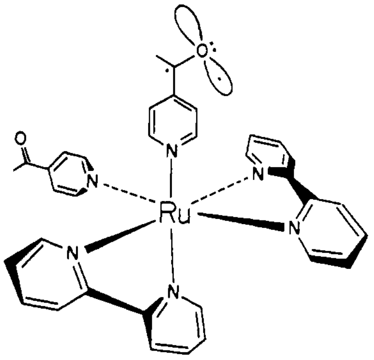
The values of $k_d$ in the table unfortunately cannot be uniformly equated with $k_{ic}$ values. Type II quantum yields of the pentaammine complexes are slightly concentration dependent. Stern–Volmer studies indicate that triplet butyrophenone is quenched by $Ru(NH_3)_5(AP)(BF_4)_2$ with a rate constant of $3 \times 10^9$ M$^{-1}$ s$^{-1}$. Therefore the IL excited states of the complexes presumably undergo some quenching by ground-state molecules, with a rate at 0.02 M of $\leq 6 \times 10^7$ s$^{-1}$. The $8 \times 10^7$ value of $k_d$ for the pentaammine complexes thus indicates that $2 \times 10^7 \leq k_{ic} \leq 8 \times 10^7$ s$^{-1}$. The value could not be much lower since the complexes do not show ketone phosphorescence at 77 K. Until more complexes have been studied, we retain our suggestion that poor overlap between carbonyl n-orbital and metal d-orbitals is responsible for the relatively slow internal conversion.[1]

The even larger $k_d$ value for the bis-bpy complex strongly suggests an additional mode of internal conversion. There are now two lower lying MLCT states and another IL state. As shown in Scheme I, we can consider conversion to the latter as internal triplet energy transfer to form locally excited triplet bpy with the discrete rate constant $k_{et}$. Since the complexed bpy molecules are nearly planar,[8] their triplet energy is about 66 kcal/mol,[9] some 4 kcal lower than that of the acylpyridines.[10] Although we cannot independently measure the extent of formation of this lower energy IL state, if we assume that $k_{ic}$ has the same value as in the pentaammine complexes, we can conclude that $k_{et} \leq 2 \times 10^8$ s$^{-1}$.

**Scheme I**



The maximum value of $k_{ic}$ is surprisingly small for exothermic, intramolecular triplet energy transfer between two organic chromophores. Rate constants are known to depend on the distance separating chormophores,[11,12] but in this case the two ligands are right next to each other. We recently have suggested that poor orbital orientation can depress rates of triplet energy transfer.[13] The present results appear to have no other ready explanation. The n-orbital of the acylpyridines is held some 6 Å away from the bpy molecules in the complex. At this distance, a rate constant near $10^8$ s$^{-1}$ might have been predicted from earlier considerations of the distance dependence of triplet energy transfer.[12] The dominance of the half-empty n-orbital in reactions involving n,π* triplets[14] thus extends even to internal energy transfer. These results further demonstrate the orbital integrity of the individual ligands complexed to ruthenium, as first shown by resonance Raman[15,16] and photoselection.[17]



We have also prepared Ru(porphyrin)$(AP)_2$ complexes with GPhBP and both octaethyl- and tetraphenylporphyrin. These also undergo type II elimination in low quantum yields, indicating that triplet energy transfer to the porphyrin ligand is also relatively slow. The ruthenium probably is not involved in any ligand–ligand energy transfer, serving merely as an expensive template. We shall investigate other metal complexes without low-lying CT excited states.

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**Registry No.** GEsBP, 106762-80-5; GPhBP, 56956-53-7; GEsBP·HCl, 106762-81-6; GPhBP·HCl, 106762-82-7; $Ru(NH_3)_5GEs$, 106762-75-8; $Ru(NH_3)_5GPh$, 106762-76-9; $Ru(bpy)_2(GEsBP)_2$, 106762-77-0; $Ru(bpy)_2(GPhBP)_2$, 106762-78-1; $Ru(OEP)(GPhBP)_2$, 106798-74-7; $Ru(TPP)(GPhBP)_2$, 106762-79-2; styrene, 100-42-5; butyl acrylate, 141-32-2.

## Photodynamic Macrocycles

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The cyclodextrins and other synthetic macrocycles have been the subject of extensive studies directed toward the synthesis of enzyme model systems.[2,3] With regard to the critical issues of product release and catalytic turnover, a conformationally dynamic system could have important advantages over these relatively static binding cavities, since the binding properties of substrate, transition state, and product could be different in the different components of a dynamic system.[4] We report herein our preliminary results with a new class of compounds that we call photodynamic macrocycles, which incorporate a spiro[pyranindoline] moiety into a carbocyclic ring. The spiro[pyranindoline]s are an important class of photo- and thermochromic compounds whose unusual properties can be attributed to the equilibrium shown in Scheme I.[5,6] The remarkable effect of the size of the carbocyclic ring on the thermodynamics of the **1a** ⇌ **1b** interconversion is the subject of this paper.

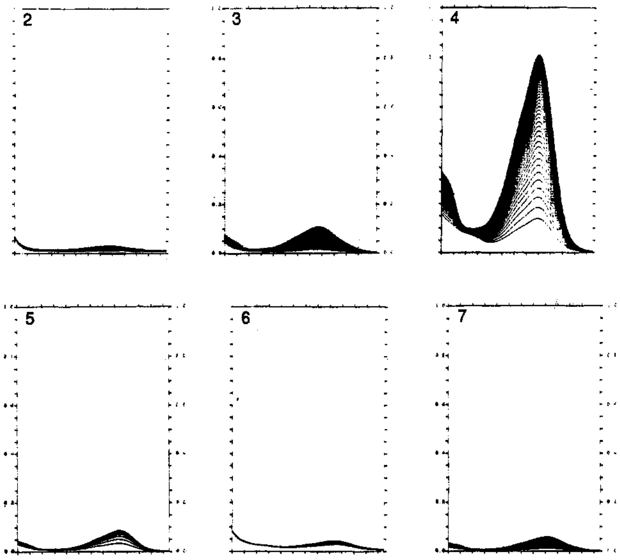


**Figure 1.**

**Scheme I**

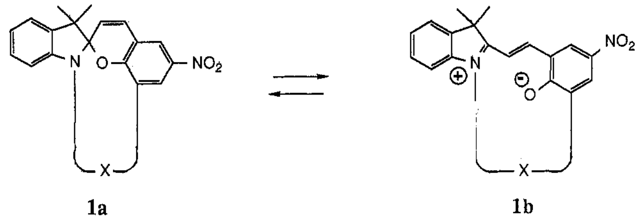
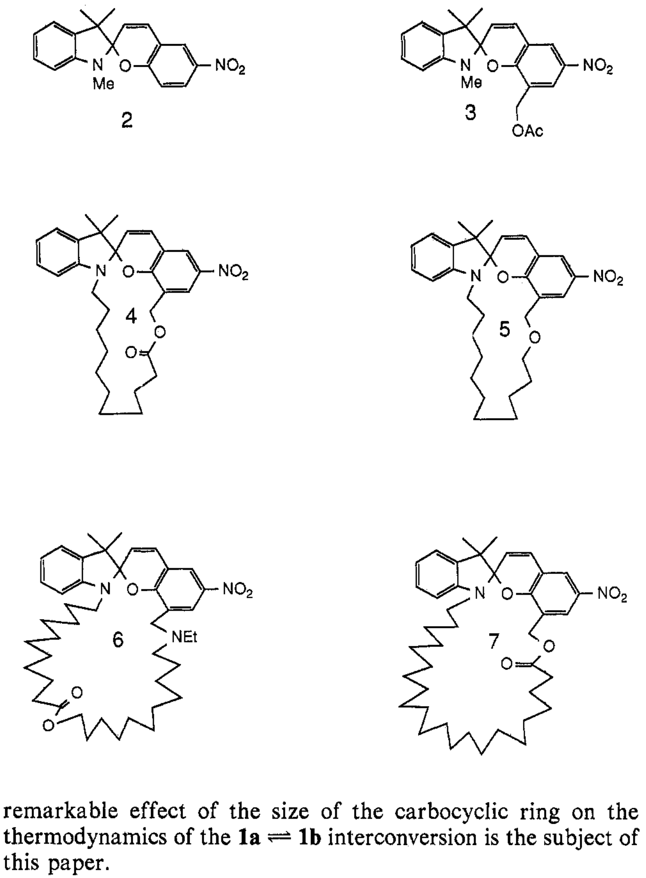


**Chart I**



To determine the effect of "X" in Scheme I on the thermal equilibrium, **1a** ⇌ **1b**, we prepared six spiro[pyranindoline]s, **2**–**7** (Chart I), to compare the behavior of **2** and **3** with the macrocyclic compounds, **4**–**7**.[7]

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(1) Recipient of a Merck Grant for Faculty Development, 1985–1986.

(2) For excellent reviews that survey the literature prior to 1984, see: (a) Diederich, F. *Nachr. Chem., Tech. Lab.* **1984**, *32*, 787–795. (b) Tabushi, I.; Yamamura, K. *Top. Curr. Chem.* **1983**, *115*, 107–159. (c) Murakami, Y. *Top. Curr. Chem.* **1983**, *115*, 107–159. (d) Breslow, R. *Science (Washington, D.C.)* **1982**, *218*, 532. (e) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. (f) Vogtle, F. *Pure Appl. Chem.* **1980**, *52*, 2405. (g) Rebek, J., Jr. *Acc. Chem. Res.* **1984**, *17*, 258.

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(4) For some recent examples, see: (a) Ueno, A.; Saka, R.; Osa, T. *Chem. Lett.* **1980**, 29. (b) Shinkai, S.; Minami, T.; Kusano, Y.; Manabe, O.; *J. Am. Chem. Soc.* **1983**, *105*, 1983. (c) Irie, M.; Kato, M. *J. Am. Chem. Soc.* **1985**, *107*, 1024. (d) Irie, M. *J. Am. Chem. Soc.* **1983**, *105*, 1246. (e) Blank, M.; Soo, L.; Wasserman, N.; Erlanger, B. *Science (Washington, D.C.)* **1981**, *107*, 3950. (f) Shinkai, S.; Inuzuka, K.; Miyazaki, O.; Manabe, O. *J. Am. Chem. Soc.* **1985**, *107*, 3950. (g) Shinkai, S.; Honda, Y.; Ueda, K.; Manabe, O. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2144. (h) Shinkai, S.; Shigematsu, K.; Honda, Y.; Manabe, O. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2879.

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