Phenyl *isocyanate* effected an analogous acylation of **1** (45 min, 20 °C, ether) resulting in a 96% yield of **7**: mp 66–67°C; NMR δ 2.18 (s, 3-CH_3), 1.00 and 3.05 (t and q, J = 7.0 Hz, 2 NCH_2CH_3), 3.73 and 3.87 (2 s, 2 OCH_3). Base-catalyzed methanolysis produced **3** + methyl *N*-phenylcarbamate. The pyrocarbonic acid system in **7** transfers its ester group to the adjacent nitrogen at 120 °C; phenyl isocyanate was removed by distillation in vacuo and the residue consisted of 98% **5** in analogy to the behavior of **4**. The high yield of the isolated adduct **7** leaves no doubt about $k_1 \gg k_2$.

On treating **1** with phenyl *isothiocyanate*, one noticed no adduct formation in the NMR spectrum. Slowly—within 4 days at 20 °C the yellow color of **1** faded—a quantitative isomerization of the 3*H*-pyrazole **1** to the aromatic 1,3-dicarboxylic ester **5** was observed. Obviously, we are dealing with a phenyl isothiocyanate catalysis. The catalyst takes over the ester group from C-3 of **1**, carries it in a conducted tour to the other side, and delivers it to the nitrogen atom.

Phenyl isothiocyanate is a weaker acylating reagent than the isocyanate; i.e., it reacts more slowly with **1**. On the other hand, the thiolcarbonic acid group in **8** exceeds the oxygen analogue **7** in acylating strength; biological acylation by acyl coenzyme A may be quoted for comparison. Thus, with phenyl isothiocyanate, formation of **8** is so slow and intramolecular acylation on N-2 to give **5** so fast that the intermediate does not become detectable ($k_1 \ll k_2$).

Kinetic experiments with NMR analysis of **1** and **5** revealed that the isomerization is first order in **1** and in phenyl isothiocyanate. The influence of solvent polarity is rather modest; 10^4k_2 (l mol^{-1} s^{-1}) at 25 °C = 1.6 in $CDCl_3$, 3.9 in benzene, 6.4 in acetonitrile, and 10.7 in nitrobenzene. It may well be that the zwitterion **2**, S^- instead of O^-, is not a discrete intermediate in the pathway to **8**.

Carbon disulfide exerts a similar, though less efficient catalysis. After 10 days at 25 °C the isomerization **1** → **5** was complete.

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(2) Satisfactory CH and N analyses were obtained for all new compounds.

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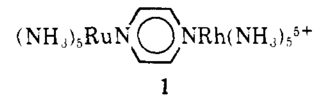
Intramolecular Energy-Transfer Reactions in Mixed Metal Dimers. $(NH_3)_5Ru^{II}LRh^{III}(NH_3)_5$

Sir:

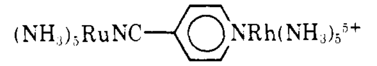
The photochemistry of unsaturated, nitrogen-coordinated, heterocyclic complexes of ruthenium(II) has been extensively studied recently.[1-5] These complexes display intense metal-to-ligand charge-transfer (MLCT) bands in the visible spectral region and, therefore, have the potential for generation of chemical potential energy from the absorption of sunlight. To convert the radiant energy into usable chemical potential energy, the absorbing molecule must either undergo direction reaction[4] or transfer its energy[6,7] or an electron[8-11] to a second, reacting molecule. These latter processes are plagued by the inefficiency inherent to bimolecular quenching processes in dilute aqueous solutions. Here we present evidence for the first intramolecular energy-transfer reaction in dilute aqueous solution using a Ru(II)–Rh(III) mixed metal dimer as a model compound.

Malouf and Ford[5] have demonstrated that $(NH_3)_5Ru^{II}L$ complexes (L = substituted pyridine or pyrazine) display MLCT maxima sensitive to L. Electron-withdrawing substituents lower the MLCT maxima and modify the photochemical reactivity of the complex. Photochemical aquation of L can be drastically reduced when the MLCT maxima is shifted below ~2.1 μm^{-1}, which places the MLCT state at an energy lower than the ^{3}LF state.[5] For this work, we have prepared and studied $(NH_3)_5Ru^{II}LRh^{III}(NH_3)_5$ complexes where the nature of L places the MLCT maxima, localized mainly on the Ru(II) fragment,[12] below 2.1 μm^{-1} to reduce possible photosubstitution reactions at Ru(II). Rh(III) was selected as the other half of the binuclear complex because the $(NH_3)_5Rh^{III}L$ monomers are known to undergo facile photoaquation reactions[13] and low temperature emission studies[13,14] enabled approximate calculations of the Rh(III) ^{3}LF excited-state energies.

The two binuclear complexes studied in this work are the pyrazine and 4-cyanopyridine Ru(II)–Rh(III) bridged dimers (**1** and **2**), respectively. The former complex has an MLCT maximum at 528 nm (1.89 μm^{-1}), while the same band for the latter complex occurs at 488 nm (2.05 μm^{-1}). The energies of these MLCT maxima are lower than 2.1 μm^{-1} and little or no photoaquation of Ru(II) is observed in either compound. In fact, extensive irradiation of the pyrazine dimer at 2.29 and 1.83 μm^{-1} leads only to a small decrease in the intensity of MLCT band, and a calculated upper limit quantum yield of 7 × 10^{-5} and 3 × 10^{-6} mol/einstein, respectively, for disappearance of starting material.



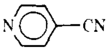
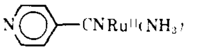
1



2

The photolysis of the 4-cyanopyridine bridged dimer differs from the pyrazine complex. The 4-cyanopyridine Rh(III) monomer and Ru(II)–Rh(III) dimer photolysis results appear in Table I. Ligand field irradiation of the Rh(III) monomer leads to cleavage of the Rh(III)–pyridine bond (Φ_L = 0.06 mol/einstein), which is characteristic of similar Rh(III) compounds.[13] MLCT irradiation of the 4-cyanopyridine bridged dimer at 436 or 546 nm (2.29 and 1.83 μm^{-1}, respectively) leads to cleavage of the same Rh(III)–pyridine bond. This photolysis reaction is not characteristic of the MLCT (Ru(II) → 4-CNpy) state and we propose that internal conversion from Ru(II) localized excited states to the reactive LF excited state associated mainly with the Rh(III) metal

Table I. Spectroscopic Quantum Yields for the Photoaquation of L from $(NH_3)_5Rh^{III}L^a$

L	E_{max} (Ru(II) → 4-CNpy, MLCT)^b	$E_{irr}{}^b$	$\Phi_L{}^c$
 CN		3.19^d	6 ± 2 × 10^{-2}
 $CNRu^{II}(NH_3)$	2.05	3.19^e	2.2 ± 0.2 × 10^{-2}
		2.29^f	3.3 ± 0.4 × 10^{-3}
		1.83^f	3.0 ± 0.3 × 10^{-4}

[a] pH 6.0. $HClO_4$ in H_2O. [b] In units of reciprocal micrometers. [c] For loss of L in units of moles/einstein. [d] Corresponds to ^1E, $^1A_2 \leftarrow {}^1A_1$ Rh(III)LF shoulder on higher energy internal ligand band. [e] Predominantly internal ligand ($\pi^* \leftarrow \pi$) character. [f] Corresponds to MLCT $\leftarrow {}^1A_1$ transition localized mainly on Ru(II) and 4-CNpy.[12]

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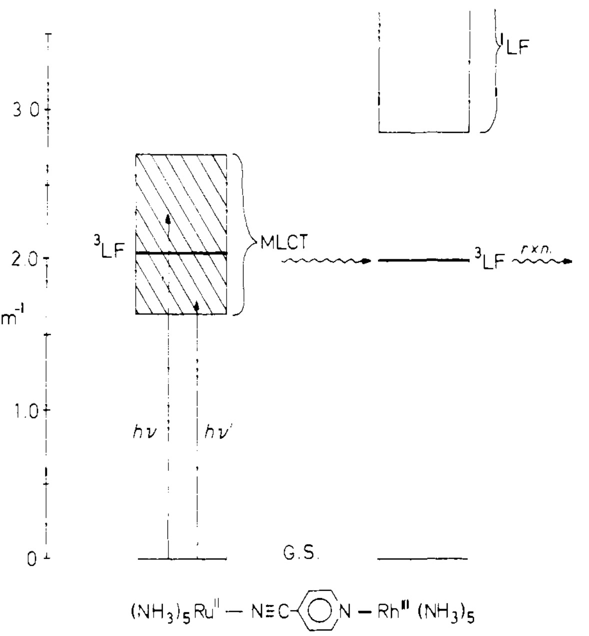


Figure 1. Proposed energy level diagram for the photolysis of **2**. Energies of excited states discussed in text.

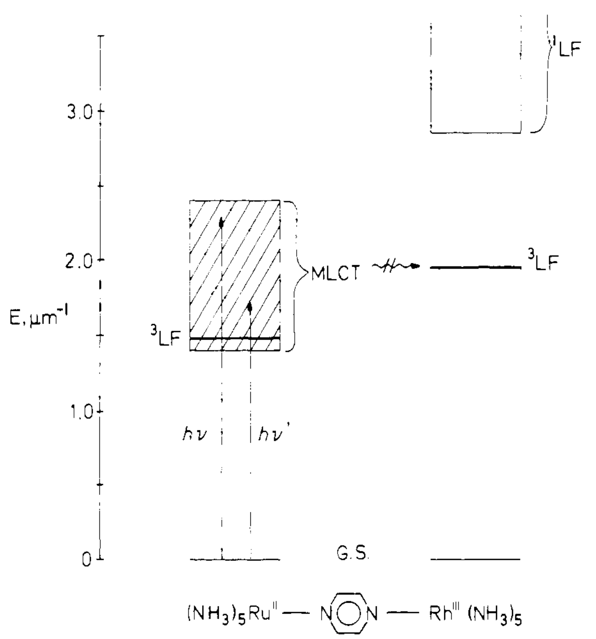
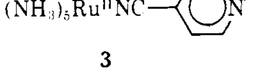


Figure 2. Proposed energy level diagram for the photolysis of **1**. Energies of excited states discussed in text.

center is responsible for the observed photoreactivity. The large error limits in Table I for the binuclear complex quantum yields are due to a secondary photolysis process. The primary photolysis products appeared to be **3** and $(NH_3)_5Rh^{III}H_2O$.



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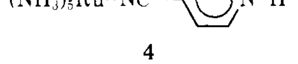


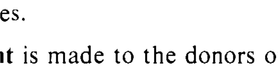
4

The former complex displays an intense MLCT band at 425 nm (2.35 μm^{-1}) and is photochemically reactive. The quantum yield for loss of 4-CNpy from the Ru(II) monomer is 1.7 × 10^{-3} mol/einstein (E_{irr} = 1.83 μm^{-1}) and 2.3 × 10^{-2} mol/einstein (E_{irr} = 2.29 μm^{-1}). Secondary photolysis can be reduced by photolyzing the dimer in pH 2.0 solution where the primary product, **4** (E_{max}(MLCT) = 1.88 μm^{-1}), has a smaller quantum yield for loss of 4-CNpyH$^+$ (3.2 × 10^{-5} and 1.5 × 10^{-3} mol/einstein for E_{irr} of 1.83 and 2.29 μm^{-1}, respectively).

Figure 1 is a simplified excited-state diagram for the 4-CNpy-bridged dimer containing the approximate energy levels of the mononuclear fragments. For Rh(III), the ^{1}LF state and the ^{3}LF state correspond to the known absorption envelope and calculated energy of the emitting excited state, respectively, for $(NH_3)_5Rhpy\text{-}X^{3+}$ complexes.[13] The ^{1}CT cross-hatched section for Ru(II) represents the observed MLCT envelope of the dimer. The Ru(II) ^{3}LF energy is approximated from the absorption spectrum of $(NH_3)_5RuN{\equiv}CCH_3^{2+}$ [15] using the singlet–triplet energy difference and triplet Stokes shift of the isoelectronic Rh(III) monomers.[13] The same type of diagram appears in Figure 2 for the pyrazine-bridged dimer. The treatment in Figure 2 is the same as discussed for Figure 1, except $(NH_3)_5Rh(pyrazine)^{3+}$ is used for the Rh(III) model and $Ru(NH_3)_6^{2+}$ [16] is used to approximate ^{3}LF for Ru(II).

Figures 1 and 2 differ in the relative energies of the Ru(II) and Rh(III) ^{3}LF states. The Rh(III) state is higher in the symmetrically bridging pyrazine case owing to larger Rh(III) d-orbital splitting (i.e., higher effective nuclear charge). We place the Ru(II) and Rh(III) ^{3}LF states at approximately the same energy for the unsymmetrically bridged 4-CNpy dimer. One explanation for the photoreactivity of the 4-CNpy dimer is that energy transfer is occurring from ^{3}LF(Ru) to ^{3}LF(Rh). Population of the ^{3}LF(Ru) state could occur by internal conversion (MLCT → ^{3}LF(Ru) which is competitive with MLCT vibrational relaxation, Boltzmann population of ^{3}LF(Ru) from thermally equilibrated MLCT, or a combination of the two. This combination could explain the wavelength-dependent quantum yield in the 4-CNpy-bridged dimer (Table I). The lack of reactivity of the pyrazine-bridged dimer would then be a result of the endothermic nature of the ^{3}LF(Ru) → ^{3}LF(Rh) process.[18]

An alternate mechanism for the 4-CNpy dimer could involve an electron-transfer process where the MLCT excited state reacts to give **5** and a labile Rh(II) fragment. Subsequent outer-sphere reverse electron transfer would presumably result in the Ru(II) product and $t\text{-}Rh(NH_3)_4(H_2O)_2^{3+}$. However, this latter mechanism does not explain the nonreactivity of the pyrazine-bridged dimer.[17]



5

The results reported here indicate that polymetallic complexes can be prepared where one metal center (e.g., Ru(II)) functions as an antenna for absorbing irradiation while a second center, in communication with the first, can undergo a chemical reaction. Also, depending on the synthetic steps involved in dimer preparation, the primary photolysis product may be a mononuclear complex which cannot be prepared by standard techniques.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

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(12) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
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(14) J. D. Petersen, Ph. D. Dissertation, University of California, Santa Barbara, 1975.
(15) R. E. Hintze and P. C. Ford, *J. Am. Chem. Soc.*, **97**, 2664 (1975).
(16) The ligand field bands for Ru(II) pyridine- and pyrazine-type complexes are obscured by the intense MLCT bands. In terms of σ basicity, py-X is more similar to NH_3 than to the nitriles.
(17) Confirming work on Ru(II)–Rh(III) dimers with other bridging ligands is currently under study both by photochemistry and cyclic voltammetry.
(18) Since calculations of the excited states give only estimated energies, we cannot eliminate the possibility of the energy transfer reaction occurring between MLCT(Ru(II)) and ^{3}LF(Rh(III)). We are currently studying bridging ligands where the MLCT maximum is at higher energy (like 4-CNpy) but the bridge is symmetrical (like pyz) to try and clarify this interpretation.

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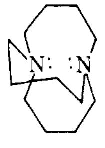
1,6-Diazabicyclo[4.4.4]tetradecane and Its Oxidized Ions

Sir:

The chemistry of medium-ring bridged bicyclic compounds is largely unexplored. While these molecules may possess many interesting properties, their uniqueness lies in the opportunities for intrabridgehead interactions. Repulsive as well as attractive interactions can be studied in these triple constrained[1] systems. In complementary fashion, the unique structural feature of propellanes is the bond common to all three rings. In particular, cleavage of this bond is an advantageous strategy for the synthesis of bridged medium-ring bicyclic compounds.[2] We have made 1,6-diazabicyclo[4.4.4]tetradecane[3] (**1**) by this route and report on its properties and those of the oxidized ions derived from it. Its protonated ions are discussed in the following communication.[4]

Reaction of 1,6-diazabicyclo[4.4.0]decane[5] with excess 1,4-dibromobutane at 100 °C furnishes the salt **4**.[6] Cyclization occurs on treatment with $AgBF_4$ in 40% aqueous HBF_4 and **3**, mp 221–225 °C dec,[6] is precipitated by the addition of EtOH. Reduction of **3** to **1** is conveniently accomplished by addition of **3** to Na/NH_3 solution, quenching with MeOH, evaporation of solvents and sublimation of **1**, mp 170–175 °C (sealed tube),[6] from the residue (84% yield). The diamine **1** and dication salt **3** react stoichiometrically in CH_3CN to give **2**, isolated by evaporation as a dark red crystalline solid.[6] This simple electron-transfer reaction is remarkably slow (k_2 = 0.2 L mol^{-1} s^{-1} at 25 °C); the rate is not much changed by the addition of 10% H_2O, but is accelerated by I^-. Study of the **1** $\rightleftharpoons$ **2** $\rightleftharpoons$ **3** system by cyclic voltammetry[7] is complicated by distended waves due to slow electron transfers especially for the **2** $\rightleftharpoons$ **3** couple. $E°$ for the **1** $\rightleftharpoons$ **2** couple is −0.1 V vs. SCE, which demonstrates the extreme ease of oxidation of **1**. These slow electron transfers may in part reflect poor overlap of the donor and acceptor orbitals.



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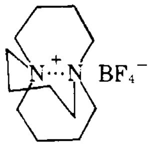

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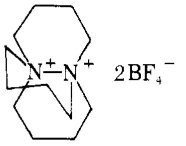

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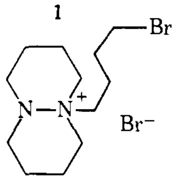

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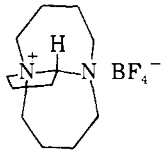

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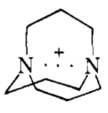

6

It is helpful to discuss the structures of **1**, **2**, and **3** in reverse order. The dication **3** is quite clearly a [4.4.4]propellane, with an all-chair, D_3, structure. The ^{1}H NMR spectrum at room temperature shows nonequivalent α-CH protons, equatorial δ 3.86 and axial δ 5.02. Coalescence occurs at +90 °C, so that the ring-flipping barrier is similar to that of the parent hydrocarbon.[8] The ^{13}C spectrum shows two resonances at −60.7 and −15.8 ppm at all temperatures. The dication salt **3** is indefinitely stable in acidic aqueous solution.

Treatment of **3** with 1 equv of aqueous K_2CO_3 gives a salt $C_{12}H_{23}N_2BF_4$, which is reducible by $LiAlH_4$ in THF to form **1**. This salt shows 11 ^{13}C NMR signals (one coincidence) with a unique CH group absorbing at −100.5 ppm and δ 5.42 in ^{1}H NMR. On the basis of the position of these signals we assign the tricyclic structure **5** to this salt, rather than the bicyclic immonium structure.

The radical cation salt, **2**, *is indefinitely stable as a solid and is stable for months in organic or aqueous solution in the absence of base.* In butyronitrile solution the ESR spectrum is a simple 15-line multiplet, unchanged between −100 and +100 °C. The intensities fit a pattern derived from hyperfine coupling to two equivalent nitrogens (a_N = 34.4 G) and six equivalent protons (a_H = 17.2 G), with a line width of 2 G. The ENDOR spectrum in CH_2Cl_2[9] shows four hydrogen hyperfine couplings of 17.8, 0.79, 0.29, and 0.08 G. Thus real or time-averaged D_3 or C_{3h} symmetry is indicated. The nitrogen hyperfine coupling is remarkably large, much bigger than in the 1,5-diazabicyclo[3.3.3]undecane radical cation **6** (14.7 G).[2b] We believe this indicates strong inward pyramidalization of the nitrogens in **2** and feel that a D_3 structure with chair-like C_4N_2 rings is probable, but with a stretched N–N distance relative to **3**.[10] The single large hydrogen splitting would then be due to the α proton equatorial to the C_4N_2 ring. The differences in nitrogen geometry between **2** and its bicyclo[3.3.3]undecane analogues[2b,11] are those which might be anticipated from the structural constraints of the hydrocarbon bridges and suggest a remarkable flexibility for the N–N interaction ("3-electron σ bond"). Despite these differences the electronic spectrum of **2** is very similar to the of **6**, consisting of one strong (oscillator strength, 0.1) and extremely broad absorption, λ_{max} 480 nm, presumably due to an $n_+(\uparrow\downarrow)$–$n_-(\uparrow)$ → $n_+(\uparrow)$–$n_-(\uparrow)$ transition.

Diamine **1** is a volatile waxy solid, notably insoluble in water and forming only weak hydrogen bonds (IR in $CDCl_3$).[12] It shows unusually strong UV absorption at λ_{max} 233 nm (ϵ 8100) with a shoulder at 261 nm (ϵ 3800) in isooctane, which either indicates flattened nitrogens, cf. manxine,[13] or some N–N interaction, or both. Out,out- or out,in-pyramidalization of the nitrogens in **1** seems improbable on this evidence. The ^{13}C NMR spectrum shows only two resonances down to −140 °C at −55.0 and −30.9 ppm, but in ^{1}H NMR nonequivalent hydrogens on the α-CH_2 groups are seen below −50 °C, indicating interconversion of D_3 or C_{3h} structures. A D_3 structure with slightly inwardly pyramidalized nitrogens and a longer N–N distance than **2** (or **3**) seems most likely. After exposure to air for 1–2 h, **1** forms an amorphous white material, insoluble in all solvents, even acids.

The isolation of all three oxidation states **1**, **2**, and **3** of the 1,6-diazabicyclo[4.4.4]tetradecane system as stable materials demonstrates the potentialities of these triply constrained

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