

complex, it is of interest to determine if the $\text{MF}_6\text{-Xe}$ system forms such complexes. The CT transition in $\text{IrF}_6\text{-Xe}$ is the closest to the ground state; thus, it is expected that the $\text{IrF}_6\text{-Xe}$ complex would be the most stable. The usual approach for determining stability of such complexes employs the method of Benesi and Hildebrand⁴ to find the equilibrium constant for complex formation. However, the near-IR data obtained for solid $\text{IrF}_6\text{-Xe}$ (Tables II and III) and the near-IR-visible data for gas-phase $\text{IrF}_6\text{-Xe}$ allow a simpler, though perhaps more approximate, alternative method to be utilized.

The fact that there is no evidence of the $\text{IrF}_6\text{-Xe}$ complex in the room temperature vapor indicates that the 1:1 complex is not strongly bound. The observed frequency shifts, increased line widths (see Table III), and intensity enhancements in the 0.1% $\text{IrF}_6\text{-Xe}$ solid samples indicate that there is significant CT interaction between IrF_6 and Xe in the ground state. However, the solid state data pertain to an $\text{IrF}_6\cdot 12\text{Xe}$ complex, whereas information on the 1:1 complex is of more intrinsic interest. Equation 1 and the assumption that the complex is weak enough to allow n' to be set equal to 12 provide an approximate relationship between the 1:12 and the 1:1 complexes.

The stabilization energy of the ground state [$12X_0(\Gamma_8(4A_2))$] of the $\text{IrF}_6\cdot 12\text{Xe}$ complex can be estimated by assuming that eq 2 can be applied to the frequency shift data for the $\Gamma_8(2T_1)$ state to find $\beta_0(\Gamma_8(2T_1))$, and that $\beta_0(\Gamma_8(4A_2))$ is roughly the same since both states stem from the $(t_{2g})^3$ configuration. These considerations lead to a value for $12X_0(\Gamma_8(4A_2))$ of $\sim 300\text{ cm}^{-1}$. The stabilization energy of the ground state $X_0(\Gamma_8(4A_2))$ of the 1:1 complex is then $\sim 25\text{ cm}^{-1}$. One would certainly expect this to be a lower limit since saturation effects⁵ have not been taken into account. The original

assumption that the ground state complex is weak thus appears well justified.

The general picture that emerges for these weak charge transfer complexes between Xe and MF_6 molecules is then as follows. The ground state is neutral probably with a shallow broad potential minimum somewhere near $r^0 \sim 4\text{ \AA}$, the Xe-Xe approximate distance in a crystal lattice or a liquid. It is possible that there are a few vibrational quanta in this well but this is not a necessary condition imposed by our data. The excited state potential well is much deeper and more narrow, and the potential minimum is such that $r^*(\text{MF}_6\text{-Xe}^+) < r^0(\text{MF}_6\text{Xe})$. These considerations also account nicely for the very broad ($> 10\,000\text{ cm}^{-1}$) Franck-Condon envelope observed for the CT transitions in all systems.

VI. Conclusion

The new electronic transitions which appear when certain transition metal hexafluorides are dissolved in liquid xenon can be assigned as intermolecular charge-transfer transitions. The concomitant charge-transfer complexes are weakly bound.

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Flash Kinetic Spectroscopic Studies of Dinuclear Rhodium(I) Complexes

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Abstract: Excitation of concentrated acetonitrile solutions of $[\text{Rh}(\text{tol})_4]\text{PF}_6$ (tol is *p*-methylphenyl isocyanide) at 562 nm, where strong absorption attributable to $[\text{Rh}_2(\text{tol})_8]^{2+}$ occurs, produces emission ($\lambda_{\text{max}} 697\text{ nm}$) with a quantum yield of 0.0065 and a lifetime of $\leq 2\text{ ns}$. Excitation of $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2$ (bridge is 1,3-diisocyanopropane) in acetonitrile solution at 553 nm gives emission at 656 nm with a quantum yield of 0.056 and a lifetime of $\leq 2\text{ ns}$. The emission is assigned to ${}^1A_{2u} \rightarrow {}^1A_{1g}$ ($2a_{1g} \rightarrow 1a_{2u}$) in both dinuclear Rh(I) complexes. Excitation also gives rise to long-lived transient absorptions attributable to the following dinuclear and trinuclear species: $\sim 8\text{ }\mu\text{s}$, $\text{Rh}_2(\text{bridge})_4^{2+}$; $0.09\text{ }\mu\text{s}$, $[\text{Rh}_2(\text{tol})_8]^{2+}$; and $0.14\text{ }\mu\text{s}$, $[\text{Rh}_3(\text{tol})_{12}]^{3+}$. In the dinuclear complexes, this transient is most likely ${}^3A_{2u}$, which is the triplet excited-state partner of ${}^1A_{2u}$. The results suggest that the spin-orbit components of ${}^3A_{2u}$ possess very little singlet character.

Introduction

In recent work it has been established²⁻⁴ that planar Rh(I) isocyanide complexes oligomerize in solution, through formation of weak metal-metal bonds. The oligomerization can be followed conveniently by monitoring electronic absorption spectra, as transitions attributable to dimers, trimers, and

higher oligomers occur at progressively lower energies. As part of our continuing study of the physical and chemical properties of Rh(I) oligomers, we have performed flash kinetic spectroscopic experiments on solutions of $[\text{Rh}(\text{tol})_4]\text{PF}_6$, where tol is *p*-methylphenyl isocyanide, and on the dinuclear complex, $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2$,³ where bridge is 1,3-diisocyanopropane.

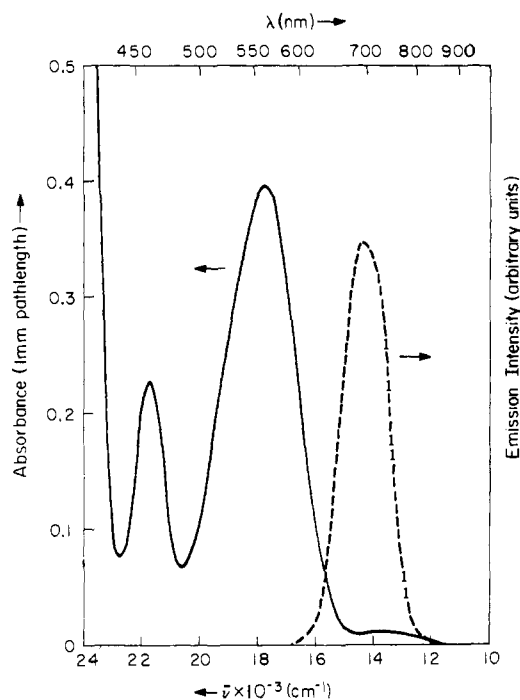


Figure 1. Absorption (—) and corrected emission (---) spectra of $[\text{Rh}(\text{tol})_4]\text{PF}_6$ in acetonitrile solution at room temperature; $[\text{Rh}]_{\text{tot}} = 4.4 \times 10^{-3} \text{ M}$.

Experimental Section

The ligands *p*-CNPhCH₃ (tol) and 1,3-diisocyanopropane (bridge)³ were prepared from the corresponding amines by standard procedures.⁵ Both ligands were purified by vacuum distillation. (Note! Several attempted distillations of bridge in which the crude product was orange resulted in violent explosions. *Extreme caution is advised.*)

$[\text{Rh}(\text{tol})_4]\text{PF}_6$. This complex was prepared by adding an excess of tol to a warm benzene solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (the latter compound was prepared by a standard procedure⁶). A precipitate formed immediately, and was filtered and washed with benzene. This precipitate was dissolved in water and a solution of KPF_6 was added. The precipitate was filtered, dried, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$: yellow crystals; $\bar{\nu}(\text{CN})$ 2160 cm^{-1} (CH_2Cl_2 solution). Anal. Calcd: C, 53.65; H, 3.94; N, 7.82; Rh, 14.36. Found: C, 53.79; H, 3.80; N, 8.03; Rh, 14.06.

$[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$. A stoichiometric amount of NaBPh_4 in methanol was added to a methanol solution of $[\text{Rh}_2(\text{bridge})_4]\text{Cl}_2$ (the latter was obtained as a blue powder by adding a stoichiometric amount of bridge to a chloroform solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$). The purple solid was then recrystallized from acetonitrile, $\bar{\nu}(\text{CN})$ 2172 cm^{-1} (KBr disk). Anal. Calcd: C, 66.37; H, 5.41; N, 10.75. Found: C, 65.59; H, 5.49; N, 10.24.

Emission Spectra. A Perkin-Elmer MPF-3A fluorescence spectrometer was employed for measurements at 25 °C in solution. All spectra were corrected for phototube and monochromator response by using a computer program that corrects raw emission data point by point. The data are then replotted either on a wavelength or an energy scale. Spectra were obtained using the standard 90° to incidence technique.

Quantum Yields. The quantum yields in undegassed fluid acetonitrile solutions at 25 °C were obtained by matching the absorbance of the sample and a reference ($\text{Ru}(\text{bpy})_3\text{Cl}_2$ in aqueous solution ($\phi = 0.042$)⁷ for $[\text{Rh}_2(\text{bridge})_4]^{2+}$; $[\text{Rh}_2(\text{bridge})_4]^{2+}$ in acetonitrile solution for $[\text{Rh}_2(\text{tol})_8]^{2+}$ at 505 nm for $[\text{Rh}_2(\text{bridge})_4]^{2+}$ and 510 nm for $[\text{Rh}_2(\text{tol})_8]^{2+}$. Spectra were then obtained as outlined above for both sample and reference under *exactly* the same instrumental conditions. The spectra were corrected and plotted on an energy scale, and the relative areas were calculated with the aid of a computer program, using the trapezoidal approximation to the area under the curve. Approximately 50 trapezoids were used for each spectrum. The ratios of the areas were taken as the ratios of the quantum yields without further correction. The error limits of $\pm 20\%$ are appropriate owing

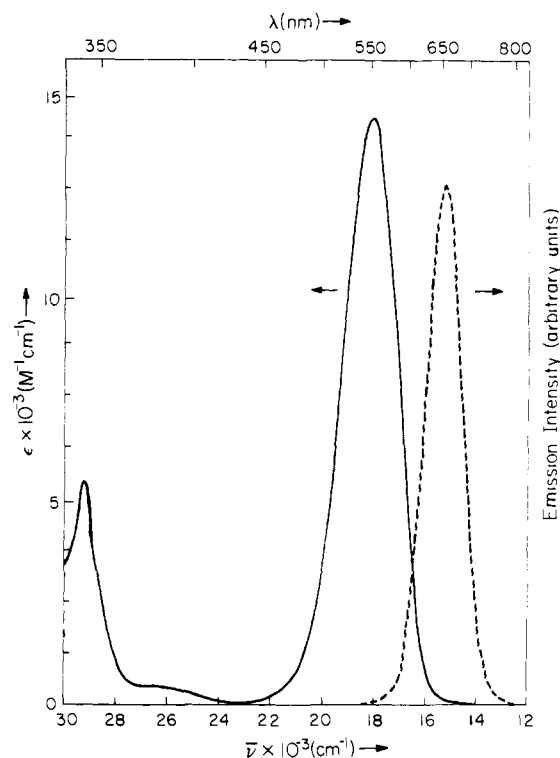


Figure 2. Absorption (—) and corrected emission (---) spectra of $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2$ in acetonitrile solution (10^{-4} M) at room temperature.

to the fact that the absorbance changes with wavelength are different for the sample and reference near the exciting wavelength.

Flash Kinetic Spectroscopic Experiments. The flash kinetic spectroscopic studies employed an apparatus that has been described previously.⁸ For the present studies, in addition to the N_2 laser (337 nm excitation), we employed the following dye lasers: Rhodamine 6G (580 nm excitation); Coumarin 495 (550 nm excitation); Nile Blue Perchlorate (705 nm excitation). The laser pulse widths were in all cases approximately 10 ns. This establishes a lower limit for measurable transient lifetimes of ~ 2 ns, as shorter lifetimes could not be deconvoluted from the laser pulse.

Samples for flash studies were degassed either by three freeze-thaw cycles or, for much of the work with $[\text{Rh}(\text{tol})_4]\text{PF}_6$ solutions, by thorough argon bubbling. Air-saturated solutions of the latter compound displayed unquenched emission, whereas transient absorption lifetimes (see Results and Discussion) were reduced approximately 40%, suggesting diffusion-controlled quenching by O_2 .

Results and Discussion

Dimer Emission. Excitation of concentrated (10^{-2} – 10^{-3} M) CH_3CN solutions of $[\text{Rh}(\text{tol})_4]\text{PF}_6$ into the dimer absorption band ($\lambda_{\text{max}} 562 \text{ nm}$) results in emission ($\lambda_{\text{max}} 697 \text{ nm}$) at room temperature.⁹ In Figure 1, we show representative absorption and emission spectra. Note that the weak absorption feature near 700 nm is attributable to trimers, whereas absorption at $\lambda < 500 \text{ nm}$ is primarily due to monomers. The emission quantum yield and lifetime were found to be 0.0065 and immeasurably short (≤ 2 ns), respectively.

Next we examined $[\text{Rh}_2(\text{bridge})_4]^{2+}$ in acetonitrile solution. Here we could employ low concentrations (10^{-5} – 10^{-4} M), as there is no evidence indicating that this dinuclear complex dissociates to monomeric species.³ Excitation into the lowest energy absorption band ($\lambda_{\text{max}} 553 \text{ nm}$) again gives emission ($\lambda_{\text{max}} 656 \text{ nm}$), as illustrated in Figure 2. The emission quantum yield was found to be 0.056. For this complex, careful scrutiny of laser excitation and emission pulse shapes suggests that the emission lifetime is near that of the laser pulse, but it is still too small to measure ($\tau \leq 2$ ns).

Table I. Values of Measured and Calculated Emission Parameters for Dinuclear Rhodium(II) Complexes in Acetonitrile Solution at Room Temperature

Complex	ϕ_F^a	τ_F , ns	k_R , s ⁻¹ ^b	τ_F , ns ^b	k_{NR} , s ⁻¹ ^b
[Rh ₂ (tol) ₈] ²⁺	0.0065	≤2	4.7 × 10 ⁷	0.14	7.2 × 10 ⁹
[Rh ₂ (bridge) ₄] ²⁺	0.056	≤2	4.3 × 10 ⁷	1.3	7.2 × 10 ⁸

^a Quantum yields are accurate to ±20%. ^b Calculated.

The latter emission quantum yield is strikingly high. We note that it is about the same as that of the "highly emissive" [Ru(bpy)₃]²⁺ ion at room temperature in fluid solution.⁷ The large overlap and small Stokes shift of the emission and absorption bands suggest that the excited state reached in absorption is also the emissive state. As the strong 553-nm absorption in [Rh₂(bridge)₄]²⁺ is attributable to the electric dipole allowed transition ¹A_{1g} → ¹A_{2u} (¹a_{2u} → 2a_{1g}),³ the emission at 656 nm is therefore assigned to "prompt fluorescence", ¹A_{2u} → ¹A_{1g} (2a_{1g} → ¹a_{2u}). An analogous assignment of the emission observed at 697 nm for [Rh₂(tol)₈]²⁺ is also suggested.

The mirror-image relationships and small Stokes shifts between the emission and absorption bands indicate¹⁰ that the theory of Strickler and Berg¹¹ can be used with confidence to calculate the radiative rate constants, k_R , that are set out in Table I. Also included in Table I are values of the emission (fluorescence) lifetime τ_F and nonradiative rate constant k_{NR} , which were calculated from k_R and the fluorescence quantum yield ϕ_F by use of the equation

$$\phi_F = \frac{k_R}{k_R + k_{NR}} = k_R \tau_F \quad (1)$$

Note that the calculated τ_F of [Rh₂(bridge)₄]²⁺ is just slightly less than our measured upper limit, reinforcing our identification of the emission as fluorescence, as a less strongly allowed radiative transition could not possibly give such a high radiative quantum yield and short lifetime.

In view of the sharp absorption and emission bands (half-widths for [Rh₂(bridge)₄]²⁺ are ~2000 cm⁻¹), it is probable that the excited state possesses a geometry that is similar to the ground state. The postulated similarity of the excited state and ground state geometries is readily explicable in terms of electronic structure. The highest occupied σ -type Rh₂ orbitals are ¹a_{1g} and ¹a_{2u}, whereas the lowest unoccupied ones are 2a_{1g} and 2a_{2u}, with the energy order ¹a_{1g} < ¹a_{2u} < 2a_{1g} < 2a_{2u}.² In the ground state, the weak Rh₂ bond arises solely from mixing of the two a_{1g} and a_{2u} orbital sets, as the lower set in each case is completely filled. However, in the lowest energy excited state an electron is removed from the antibonding ¹a_{2u} orbital; thus, the excited state has a formal d_{x²-y²}-d_{z²} Rh₂ bond order of 1/2. Furthermore, the excited electron occupies a formally p_z-p_z Rh₂ bonding orbital, 2a_{1g}. The excited state should therefore be slightly more strongly Rh₂ bound than the ground state, whereas metal-ligand bonding should be little affected.¹²

The absorption and emission bands of [Rh₂(tol)₈]²⁺ are both about 20% broader than those of [Rh₂(bridge)₄]²⁺, and the Stokes shift is larger (3450 vs. 2840 cm⁻¹). This larger Stokes shift suggests that the relaxed excited state of [Rh₂(tol)₈]²⁺ is more distorted than that of [Rh₂(bridge)₄]²⁺. Despite the broader bands of [Rh₂(tol)₈]²⁺, the radiative rate constant is calculated to be about the same as that of [Rh₂(bridge)₄]²⁺ (Table I), and the roughly tenfold smaller ϕ_F therefore implies that k_{NR} must be about ten times larger for the tol complex. Further discussion of k_{NR} will be presented below.

Long-Lived Transients. Excitation of solutions containing [Rh₂(tol)₈]²⁺ and [Rh₂(bridge)₄]²⁺ gives, in addition to the prompt fluorescence, long-lived transient absorption. Figure

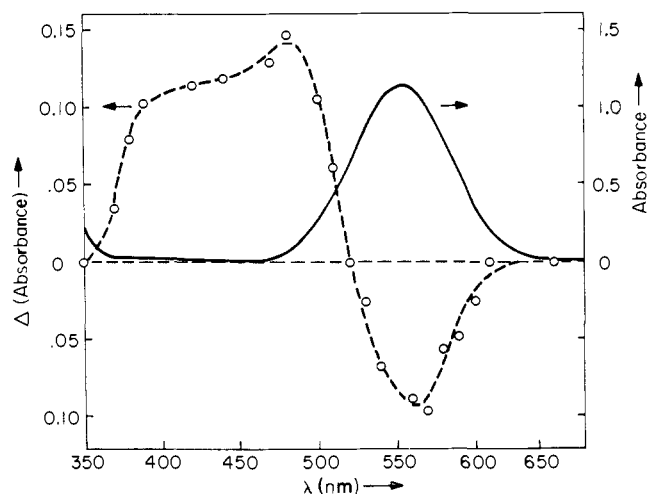


Figure 3. Absorption (—) and transient difference (---) spectra (550 nm excitation) of [Rh₂(bridge)₄](BPh₄)₂ in acetonitrile solution (8 × 10⁻⁵ M) at room temperature; path length = 1 cm.

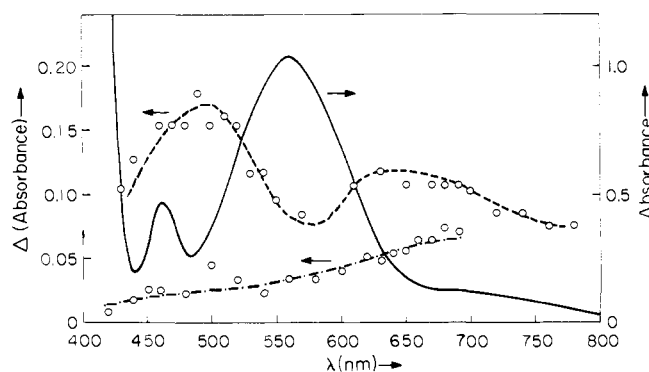


Figure 4. Absorption (—) and transient difference (580 nm --- and 705 nm - - -) excitation spectra of [Rh(tol)₄]PF₆ in acetonitrile solution at room temperature; [Rh]_{tot} = 8 × 10⁻³ M; path length = 1 mm.

3 shows the transient spectrum obtained for [Rh₂(bridge)₄]²⁺. Decay of the transient is first order at all wavelengths, and the lifetime is $\tau_T = 8 (\pm 4) \mu\text{s}$.

The transient spectrum shows bleaching of the ground state absorption between 500 and 600 nm. From the known laser pulse intensity, we have calculated a lower limit for the quantum yield of formation of the transient by assuming that it does not absorb at 560 nm, arriving at $\phi_T \approx 0.8$. The actual value is probably higher. In any case, it is clear that the long-lived transient accounts for most, if not all, of the absorbed photons that do not lead to prompt fluorescence.

In view of the first-order decay, the long-lived transient is most likely another molecular excited state, and the only reasonable possibility is the triplet state (³A_{2u}) associated with ¹a_{2u} → 2a_{1g} excitation. The moderately intense transient absorption (calcd ϵ 's are 1–2 × 10⁴ M⁻¹ cm⁻¹) could correspond to transitions terminating in the ¹a_{2u} hole of this excited state; the dinuclear Rh(II) complexes, [Rh₂(bridge)₄X₂]²⁺, show intense absorptions in this region that have been assigned to such transitions.³

The [Rh₂(tol)₈]²⁺ complex exhibits similar transient absorption (Figure 4), but with somewhat more complicated behavior. Our initial experiments using 580-nm laser excitation showed some variation of transient lifetime with both rhodium concentration and monitoring wavelength, with the lifetimes evaluated near 700 nm being longer than those at shorter wavelengths and increasing with increasing concentration. The disparity was greatly decreased when we employed 550-nm

laser excitation, and consistent lifetimes were obtained, $\tau_T = 0.09 (\pm 0.01) \mu\text{s}$.

When we employed 705-nm excitation (which falls in the region of a trimer absorption band),² a completely different transient absorption spectrum was observed (Figure 4), with a longer lifetime, $\tau_T = 0.14 (\pm 0.01) \mu\text{s}$. We conclude that this transient is the excited triplet of $[\text{Rh}_3(\text{tol})_{12}]^{3+}$, and that 580-nm laser excitation gives some simultaneous excitation of ground state trimers, especially at the higher concentrations.

We observed no evidence for quenching or excimeric interactions of ground state monomers with the transients. However, because of the overlapping absorption of the two transients and our limited useful concentration range (10^{-2} – 10^{-3} M), our sensitivity for detection of such processes was not very high. An estimate of the quantum yields of formation of the triplets of $[\text{Rh}_2(\text{tol})_8]^{2+}$ and $[\text{Rh}_3(\text{tol})_{12}]^{3+}$ cannot be made from our data, as the transient absorption spectra are broader than those of the triplet state of $[\text{Rh}_2(\text{bridge})_4]^{2+}$, and ground state bleaching is less well defined. However, the yields must be similarly high, in view of the large $\Delta(\text{OD})$'s.

From the overlap of the $[\text{Rh}_2(\text{bridge})_4]^{2+}$ fluorescence and absorption spectra, we estimate that the 0–0 energy of the ${}^1A_{1g} \rightarrow {}^1A_{2u} (1a_{2u} \rightarrow 2a_{1g})$ transition is $\sim 16\,500 \text{ cm}^{-1}$. If the singlet–triplet splitting is similar to that of the isocyanide monomers,² then the 0–0 energy of the ${}^1A_{1g} \rightarrow {}^3A_{2u} (1a_{2u} \rightarrow 2a_{1g})$ transition should be at $\sim 13\,500 \text{ cm}^{-1}$. However, no trace of an absorption band was observed between 15 000 and 10 000 cm^{-1} , and we estimate that the ϵ_{max} of any peak in this energy region cannot be more than about 100. This is in striking contrast to the situation observed in the monomeric Rh(I) complexes,² where the ${}^1A_{1g} \rightarrow E_u({}^3A_{2u})$ band has over one-tenth as much intensity as ${}^1A_{1g} \rightarrow {}^1A_{2u}$, suggesting that $E_u({}^3A_{2u})$ has acquired considerable singlet character through spin–orbit mixing with higher $E_u({}^1E_u)$ states. The low intensity of the singlet–triplet band in $[\text{Rh}_2(\text{bridge})_4]^{2+}$ indicates that such singlet–triplet mixing is much smaller, in complete accordance with the low values we have observed for spin-forbidden nonradiative decay rates.

The very small singlet character of ${}^3A_{2u}$ in $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is attributable to the fact that the lowest energy $E_u({}^1E_u)$ state is far removed from $E_u({}^3A_{2u})$. Thus, spin–orbit mixing of the E_u component of ${}^3A_{2u}$ with the $E_u({}^1E_u)$ state would be expected to be much smaller than in the monomeric systems, where the parent states lie close together.¹³ An interesting trend is observed in the two dinuclear Rh(I) complexes, namely, that the lifetimes of both the ${}^1A_{2u}$ and ${}^3A_{2u}$ excited states are substantially shorter for $[\text{Rh}_2(\text{tol})_8]^{2+}$. If our pre-

ceding conjectures are correct, then the singlet character of the ${}^3A_{2u}$ excited state must be larger in $[\text{Rh}_2(\text{tol})_8]^{2+}$ than in $[\text{Rh}_2(\text{bridge})_4]^{2+}$.

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- (9) This emission is not due to an excited monomer. Glassy solutions (EPA) of $[\text{Rh}(\text{CNPh})_4]\text{PF}_6$ at ~ 80 K exhibit a moderately intense emission peaking at 580 nm. The emission band shows a mirror-image relationship to the absorption band at 468 nm,² and the emission excitation and absorption spectra are in good agreement between 300 and 500 nm. As it has been established² that this absorption band is due to the MLCT transition ${}^1A_{1g} \rightarrow E_u({}^3A_{2u}) (a_{1g}(d_{z^2}) \rightarrow a_{2u}(p_z, \pi^*(\text{CNPh}))$), the emission must be $E_u({}^3A_{2u}) \rightarrow {}^1A_{1g}$. It may also be noted that monomeric Rh(I) phosphine complexes exhibit emission spectra in low temperature glasses that apparently involve the same type of excited state [G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 3105 (1974)]. However, we have not observed electronic emission from solutions containing monomeric $[\text{Rh}(\text{CNPh})_4]^+$ at room temperature. Furthermore, dilute CH_3CN and CH_2Cl_2 solutions of $[\text{Rh}(\text{tol})_4]\text{PF}_6$, which contain only monomers, do not exhibit emission or transient absorption, nor do they undergo photochemical reactions upon irradiation at 337 nm, a wavelength of intense monomer absorption. Irradiation at 337 nm of concentrated CH_3CN solutions, which contain dimers as well as higher oligomers, leads to very weak transient absorption and emission spectra. These latter spectra are identical with those obtained upon irradiation into dimer absorption bands.
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- (12) The reason that the excited state in question is more energetic than ${}^1A_{1g}$ is that the C \equiv N bonds are weakened, owing to the $\pi^*(\text{C}\equiv\text{N})$ participation in $2a_{1g}$.
- (13) The absorption spectrum of $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$ in acetonitrile solution exhibits intense bands at 29 100 (ϵ 5450) and 31 500 cm^{-1} (ϵ 45 400), in addition to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ peak at 553 nm (18 000 cm^{-1} , ϵ 14 500). The 29 000 and 31 500 cm^{-1} bands may be assigned to ${}^1A_{1g} \rightarrow E_u({}^3E_u)$ and ${}^1A_{1g} \rightarrow E_u({}^1E_u)$, respectively, and the peak maximum of ${}^1A_{1g} \rightarrow E_u({}^3A_{2u})$ should fall at about 15 000 cm^{-1} . The estimated 16 500- cm^{-1} separation between $E_u({}^3A_{2u})$ and $E_u({}^1E_u)$ in $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is therefore much larger than the corresponding splitting of about 9500 cm^{-1} in each of several $[\text{Rh}(\text{CNR})_4]^+$ monomers [K. R. Mann, Ph.D. Thesis, California Institute of Technology, 1977; H. Isci and W. R. Mason, *Inorg. Chem.*, **14**, 913 (1975)].