$$[\mathrm{Rh_2(dimen)_2(dppm)_2}]^{2+} \rightleftharpoons [\mathrm{Rh_2(dimen)_2(dppm)_2}]^{3+} + e^- \tag{1}$$

$$[\mathrm{Rh_2(dimen)_2(dppm)_2}]^{3+} \rightleftharpoons [\mathrm{Rh_2(dimen)_2(dppm)_2}]^{4+} + e^- \tag{2}$$

$$[\mathrm{Rh_2(dimen)_2(dppm)_2}]^{4+} + nX^- \rightleftharpoons [\mathrm{Rh_2(dimen)_2(dppm)_2(X)}_n]^{(4-n)+} \tag{3}$$

$$X^- = \mathrm{PF_6}^-, \mathrm{ClO_4}^-; n = 1, 2$$

The quasi-reversible nature of the first oxidation process suggested that the electrochemical generation of bulk concentrations of $[Rh_2(dimen)_2(dppm)_2]^{3+}$ might be feasible. Green solutions of the stable $d^7$–$d^8$ radical $[Rh_2(dimen)_2(dppm)_2]^{3+}$ are conveniently generated via bulk electrolysis of $[Rh_2(dimen)_2(dppm)_2]^{2+}$ solutions at 0.8 V. Solutions containing ~1 mM concentrations of the electrode reaction product are stable for days under an Ar atmosphere.[25] Oxidation at +0.8 V at an optically transparent thin-layer electrode (OTTLE)[26] results in the spectral changes summarized in Figure 2. The absorbances at 322 and 565 nm decrease in intensity while new absorbances appear as the electrolysis proceeds. The similarities between the spectrum of the electrogenerated species ($\lambda_{max}$ = 448 nm, $\epsilon = 3.78 \times 10^4$ $M^{-1}$ $cm^{-1}$; $\lambda_{max}$ = 647 nm, $\epsilon = 2.50 \times 10^3$ $M^{-1}$ $cm^{-1}$) and the transient absorbance spectrum of $[Rh_2(bridge)_4]^{3+}$ previously obtained[2] ($\lambda_{max}$ = 438 nm, $\epsilon = 3.45 \times 10^4$ $M^{-1}$ $cm^{-1}$; $\lambda_{max}$ = 705 nm, $\epsilon = 2.00 \times 10^3$ $M^{-1}$ $cm^{-1}$) are striking and indicate that both spectral bands are associated with transitions that are predominantly metal-localized. We tentatively assign the intense, higher energy feature to the $d_{\sigma_b} \rightarrow d_{\sigma^*}$ transition and the weaker, lower energy feature to a $d_{\sigma^*} \rightarrow p_\sigma$ one-electron excitation.[27]

Further characterization of the electrogenerated species as a $d^7$–$d^8$ metal–metal bonded radical species is obtained from the X-band EPR spectrum exhibited by the green solution. As shown in Figure 4, two signals[28] are observed in the EPR spectrum of the radical species in $CH_2Cl_2$/TBAP at −165 °C. The observation of two different *g* values for the $D_{2h}$ radical under these conditions is consistent with their random orientation with respect to the applied magnetic field. The assignment of the signal with $g$ = 1.99 that exhibits a three-line pattern due to hyperfine coupling to two equivalent Rh atoms ($A = 19.77 \times 10^{-4}$ $cm^{-1}$) to the *g* value of the metal–metal principal axis is consistent with similar EPR signals observed for other binuclear Rh(I)–Rh(II) radicals previously reported.[29] The signal at $g$ = 2.21 exhibits a five-line pattern ($A = 18.05 \times 10^{-4}$ $cm^{-1}$) and is tentatively assigned to the $Rh_2P_4$ principal magnetic axis. A third, unsplit signal expected for the $Rh_2(CN)_4$ principal magnetic axis is likely under the $Rh_2P_4$ signal. We have observed similar EPR spectra for other related $d^7$–$d^8$ complexes. A more complete analysis of the EPR spectra of these radicals will be the subject of a later report.

The three-line pattern observed for the *g* value of the Rh–Rh principal magnetic axis indicates that the unpaired electron is delocalized on the EPR time scale, with equal amounts of unpaired spin density on two equivalent Rh centers. The rate of electronic delocalization is also suggested to be fast on the more rapid infrared time scale. The infrared spectrum of the radical species exhibits a single, sharp $\bar{\nu}$(CN) stretching frequency at a relatively high value of 2174 $cm^{-1}$. The high value for the $\bar{\nu}$(CN) stretch observed for this radical is consistent with a substantial decrease in electron density at Rh in the radical and the relatively high, positive reduction potential for this species.

We have barely begun to investigate the chemical reactivity of the radical species, but several interesting observations of chemical reactivity have been made. In contrast to the photolytically generated $d^7$–$d^8$ $[Rh_2(bridge)_4]^{3+}$ radical that dimerizes at a rate ($k \approx 10^7$ $M^{-1}$ $s^{-1}$) approaching the diffusion limit, $[Rh_2(dimen)_2(dppm)_2]^{3+}$ shows no observable propensity to dimerize on a scale of several days. However, the $[Rh_2(dimen)_2(dppm)_2]^{3+}$ radical rapidly undergoes disproportionation[30] in the presence of ligands that stabilize the Rh(II)Rh(II) binuclear oxidation state. For example, the addition of $Cl^-$ (benzyltriethylammonium chloride) to a $CH_2Cl_2$ solution of $[Rh_2(dimen)_2(dppm)_2]^{3+}$ results in a nearly instantaneous color change of the solution from green to red, the result of a rapid, net disproportionation as determined by UV–vis spectroscopy:

$$2\mathrm{Rh}^{\mathrm{I}\,1/2}\mathrm{Rh}^{\mathrm{I}\,1/2} \xrightarrow{\mathrm{Cl}^-} \mathrm{Rh^IRh^I} + \mathrm{Rh^{II}Rh^{II}} \tag{4}$$

On the basis of the observation of this reaction, we speculate that the previously studied, net photolytic 2e reduction of $H^+$ to $H_2$ may result via the formation of $[Rh_2(bridge)_4]^{2+}$ through $[Rh(bridge)_4]^{3+}$ radical disproportionation. This hypothesis is attractive because it is consistent with the low quantum yield observed for hydrogen generation in the $[Rh_2(bridge)_4]_2^{6+}$ system under highly acidic conditions. A ligand-induced disproportionation rate for $[Rh_2(bridge)_4]^{3+}$ that is slow relaive to the fast ($10^7$ $M^{-1}$ $s^{-1}$) radical dimerization rate would lead to the low quantum yield. Further studies designed to test the involvement of $d^7$–$d^8$ radical species in thermal and photochemical reactions of $d^8$–$d^8$ binuclears are currently in progress in our laboratory.

**Acknowledgment.** We thank Gary Rodman for several helpful discussions, Brian Johnson for assistance with the $^{31}P$ NMR spectra, Prof. J. D. Britton for his assistance in the X-ray structure determination, and Johnson-Matthey, Inc., for a generous loan of rhodium trichloride.

**Supplementary Material Available:** Listings of atomic coordinates and general temperature factors for $[Rh_2(dimen)_2(dppm)_2](PF_6)_2$ (4 pages). Ordering information is given on any current masthead page.

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*Received April 4, 1986*

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(25) Cyclic voltammetric scans of the bulk electrolyzed solution initiated from +0.8 V toward less positive potentials exhibit the quasi-reversible 1e wave.

(26) The OTTLE consisted of a 100 line/in. gold minigrid electrode (Buckbee-Mears) sealed beteween quartz plates with Tefzel fluoropolymer (E. I. DuPont de Nemours & Co.). The gas-tight apparatus had a path length of 180 μm.

(27) A reviewer has pointed out that the decrease in intensity of this band may not be consistent with its assignments as the $d_{\sigma^*} \rightarrow p_\sigma$ of the $Rh_2^{3+}$ core. Our tentative assignment is based on the slight shift to lower energy as compared with that of the $Rh_2^{2+}$ compound. Perhaps the decrease in intensity is the result of a smaller transition moment integral.

(28) The relatively small deviations of the *g* values of this radical from the free-electron value are consistent with the electron occupying a $\sigma_b$ or $\sigma^*$ orbital. See: Kawamura, T.; Fukamachi, K.; Sowa, T.; Hayashida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *105*, 364.

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(30) The mechanism for the disproportionation reaction 4 may involve the binding of $Cl^-$ to an axial site of the $[Rh_2(dimen)_2(dppm)_2]^{3+}$ radical as the rate-limiting step. The resulting radical species ($[Rh_2(dimen)_2(dppm)_2Cl]^{2+}$) is equivalent to the 19e putative intermediates that have been postulated for photochemical disproportionation reactions of $[CpMo(CO)_3]_2$. See: Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4055. Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032.

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## MCPL Evidence for the Transition from Delocalized to Localized Luminescent States of $Ru(bpy)_3^{2+}$ in Glass–Fluid Media

*Sir:*

There has been considerable debate about the characterization of the luminescent states of $Ru(bpy)_3^{2+}$.[1-13] The central issue

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is whether the electronic charge on the ligands is localized on one ligand or delocalized across the three ligands. Excited-state resonance Raman scattering in fluid solutions can only be interpreted with a localized model, but measurements in a number of solid phases[13] reveal an entirely different excited-state Raman profile. MCPL measurements[12] made with crystals below 60 K and other polarized spectroscopic measurements require a delocalized interpretation. Our reconciliation[9] of these conflicting lines of evidence has been criticized by Danielson et al.,[14] who suggested that the spectral changes, which occur during the fluid–glass transition, are due solely to solvent dipole reorientation effects. We report here measurements of MCPL that demonstrate the transition from delocalized to localized emission in fluid media, a process occurring over a similar temperature range *but distinct from the solvent dipole process*, confirming our earlier work.[9]

Steady-state and time-resolved luminescence spectra establish that over the region of temperature 125–140 K in ethanol/methanol (4:1) there are both shifts and *profile changes* in the luminescence spectra.[9] About 20% of the apparent overall shift of the emission band is due to a change in spectral distribution, which also encompasses a change in the vibronic structure. Analogous spectral changes were observed for the glass-forming mixture proprionitrile/butyronitrile (4:5) but over a slightly lower temperature range.

As well as spectral profile differences in the spectra of the two species, we expect to observe very different behavior in their magnetically circular-polarized luminescence (MCPL) properties. The delocalized species ($D_3$ symmetry) will have a number of E states with nonzero magnetic $g$ factors, so that $C$ term behavior can be expected. On the other hand, a transition to a localized species ($C_2$ symmetry) should lead to a significant reduction of the MCPL signal, as only magnetically induced mixing components ($B$ terms), can then arise. $B$ terms have a magnitude (relative to that of $C$ terms) of $kT/\Delta E$, where $\Delta E$ is the separation of electronic levels mixed by the field. $B$ terms do not show the $1/T$ temperature dependence of $C$ terms, and as $\Delta E$ has magnitude of 100 cm$^{-1}$ for Ru(bpy)$_3^{2+}$, $B$ and $C$ terms may become comparable for $T > 100$ K.

Between about 10 and 120 K there is a substantial temperature-dependent MCPL signal from Ru(bpy)$_3^{2+}$ in ethanol/methanol (4:1), analogous to that observed in PVA.[15] We found no similar temperature-dependent MCPL for the diethyl ester of Ru(bpy)$_2$(bpy-4,4′(COOH)$_2$)$^{2+}$ measured under identical conditions in ethanol/methanol solution, weaker signals being observed.[16] This complex has been thought to be localized in its luminscent state.[17] The MCPL signal observed for Ru(bpy)$_3^{2+}$ drops markedly through the glass–fluid transition (Figure 1). It is important to compare these MCPL data with those observed in other phases over the same temperature range. The magnitude of the MCPL observed in the glassy phase (120 K) in Figure 1 is almost identical with those observed in single crystals of Zn(bpy)$_3$(BF$_4$)$_2$, as well as in PVA films where the species forms a true solid solution.[14] Figure 2 shows the same phenomenon in

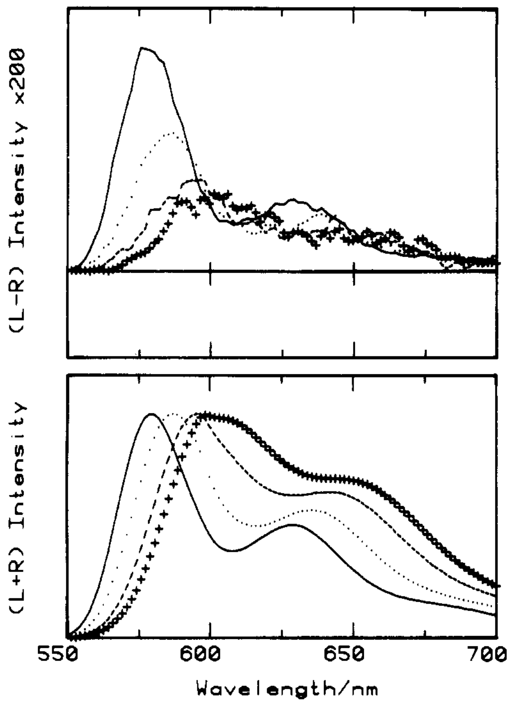

**Figure 1.** MCPL (top) and total luminesence (bottom) of Ru(bpy)$_3^{2+}$ in 4:1 ethanol/methanol. The concentration was 2.5 × 10$^{-4}$ M as the chloride salt, and excitation was provided by polarization-scrambled light at 458 nm from an Ar$^+$ laser. The applied magnetic field is 4 T, and the temperatures are 120 K (—), 130 K (···), 135 K (– –), and 140 K (+++). Individual luminescence spectra have not been corrected for system response but have been normalized to the peak-detected value to allow direct comparison of the MCPL ratios. The MCPL spectrum at each temperature is correspondingly scaled to the luminescence. Thus, variations in the ratio (L − R)/(L + R), with L and R being the detected intensities of left and right circularly polarized light, are observed directly.

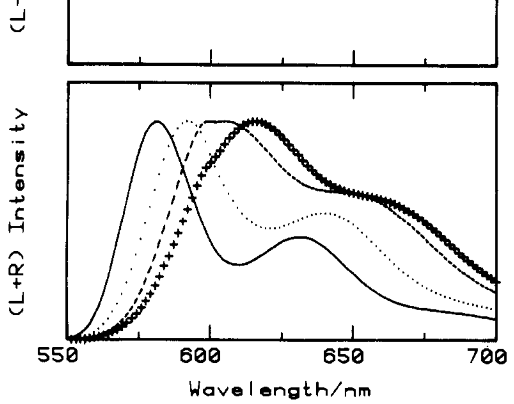

**Figure 2.** MCPL (top) and total luminescence (bottom) of Ru(bpy)$_3^{2+}$ in 4:5 propionitrile/butyronitrile. The concentration was 5 × 10$^{-4}$ M as the PF$_6$ salt. The temperatures are 110 K (—), 120 K (···), 125 K (– –) and 137 K (+++). Other details are as in Figure 1.

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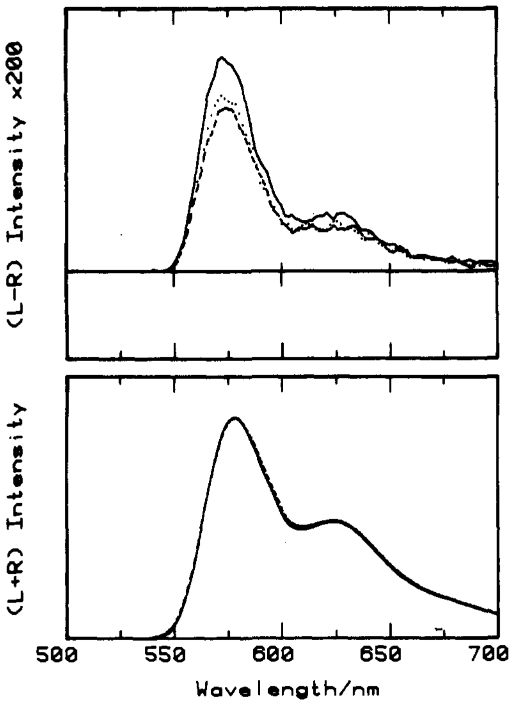

**Figure 3.** MCPL (top) and total luminescence (bottom) of $Ru(bpy)_3^{2+}$ in poly(vinyl alcohol) film. The concentration was $5 \times 10^{-4}$ M, dissolved as the chloride salt. The temperatures are 120 K (—), 130 K (···), and 137 K (– –). Other details are as in Figure 1.

the 4:5 propionitrile/butyronitrile system occurring about 10 K lower in temperature. Figure 3 shows the MCPL of $Ru(bpy)_3^{2+}$ in PVA over the same temperature range as in Figure 1. A small decrease in intensity of the MCPL is seen, and measurements taken over a wider temperature range reveal basically $1/T$ ($C$ term) behavior.[14]

The interpretation of the MCPL data in Figures 1 and 2 is straightforward. The marked drop in the MCPL signal, from that observed in the glass phase to that observed in the liquid phase, is exactly the behavior we expect for a transition from a delocalized to a localized species. Measurements taken at higher temperatures reveal little further reduction in the MCPL, consistent with a residual $B$ term. Figure 4 shows a comparison of the shift of the luminescence maximum and the MCPL strength derived from the data in Figure 1 for the 4:1 ethanol/methanol solvent system. This clearly shows that the localization process occurs more quickly than the solvent dipole relaxation process. The relative rates of shift and localization, both distinct as revealed by the MCPL, occur at *different* rates in the two solvent systems studies. The details of the spectra depend slightly on the thermal history of the sample and the concentration of the cation used, but the basic phenomenon as revealed in Figures 1, 2, and 4 is repeated in each case. In the 4:5 propionitrile/butyronitrile system, the MCPL drops even more quickly compared to the shift of the luminescence maximum.

We have considered the possibility that part of the reduction of the MCPL is due to the photoselection process[15] but conclude that only a small fraction of the reduction can arise from this mechanism.

The dependence of the MCPL reduction phenomenon on the temperature range of the glass–fluid transition and its absence in PVA and single crystal[15] establishes that the localization is not intrinsic at 100 K and must involve either solvent reorientation or counterion reorientation. The fact that the localization does not follow the solvent dipole reorientation behavior suggests that the driving force may be counterion reorientation, but this matter needs further detailed investigation.

We are currently analyzing these data quantitatively, along with lifetime and time-resolved luminescence measurements, which along with MCPL measurements completely substantiate our viewpoint. The interpretation of the MCPL reduction can be put independently by using the simple qualitative arguments given.

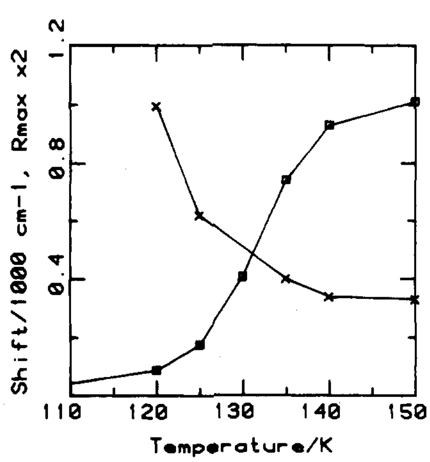

**Figure 4.** Shift of the luminescence maximum (obtained from corrected spectra) of $Ru(bpy)_3^{2+}$ in 4:1 ethanol/methanol (Figure 1) (□) from its position at 100 $K$ and $R_{max}$ and ratio of the peak MCPL to the peak luminescence (×).

**Acknowledgment.** We thank Professor Meyer for a copy of ref 14.

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*Received April 3, 1986*

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## A Bimetallic Ruthenium Hydride Borohydride Complex with Unusually Short Ruthenium–Boron Distances. X-ray Crystal Structure of $[(tripod)HRu(\mu,\eta^2\text{-}BH_4)RuH(tripod)]BPh_4$ (tripod = $MeC(CH_2PPh_2)_3$)

*Sir:*

The coordination modes of the tetrahydroborate ligand $BH_4^-$ in transition-metal complexes have been shown to be quite versatile, adopting unidentate,[1] bidentate,[2] and tridentate[2] coordination. Although numerous examples exist in the extant literature of $BH_4^-$ bound to a single metal, cases in which $BH_4^-$ bonds to more than one metal are rare.[3] The first example of a bimetallic group 8 tetrahydroborate complex with a $\mu,\eta^2$-$BH_4^-$ ligand is now reported.[4]

Treatment of a yellow $CH_2Cl_2$ solution of $RuH(BH_4)(tripod)$ (**1**)[5] with MeOH at room temperature results in a darkening in color with concomitant evolution of gas. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicates quantitative conversion to a single cation, **2**, showing a singlet at $\delta$ +39.33. Salts containing cation **2** can be isolated from MeOH solution with $BF_4^-$,

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(4) Recently, Fehlner and co-workers reported a trinuclear iron compound in which $BH_4^-$ bonds in a $\mu,\eta^3$-manner: Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.

(5) Compound **1** was prepared by reaction of $NaBH_4$ and $[Ru(tripod)(MeCN)_3](CF_3SO_3)_2$ in MeOH, which in turn was synthesized by treatment of $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$ with 4 molar equiv of $AgCF_3SO_3$ in acetonitrile. (See also: Crabtree, R. H.; Pearman, A. J. *J. Organomet. Chem.* **1978**, *157*, 335.)