

Communications

Preparation, Characterization, and Oxidation Chemistry of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2](\text{PF}_6)_2$ (dimen = 1,8-Diisocyanomenthane; dppm = Bis(diphenylphosphino)methane). Electrochemical Generation of a Stable d^7-d^8 Radical

Sir:

In 1977 it was reported that visible light photolysis of hydrochloric acid solutions of the tetranuclear rhodium complex $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ (bridge = 1,3-diisocyanopropane) results in the two-electron oxidative cleavage of the metal complex into $[\text{Rh}_2(\text{bridge})_4\text{Cl}_2]^{2+}$ with the concomitant reduction of protons to hydrogen gas.¹ Flash photolysis studies of the tetranuclear species in sulfuric acid solutions indicated that the primary photolytic step is excited-state cleavage of the central Rh-Rh interaction to highly reactive $[\text{Rh}_2(\text{bridge})_4]^{3+}$ d^7-d^8 radicals.² Although mechanistic studies³ suggested that $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is the proton reductant in these aqueous acid solutions, the mechanistic details of the reactions that couple the photolytic formation of $[\text{Rh}_2(\text{bridge})_4]^{3+}$ d^7-d^8 radicals to hydrogen generation are unknown. Toward understanding this reaction mechanism and the general thermodynamic and kinetic properties required of a system to undergo net multielectron-transfer reactions,⁴ we have set out to generate and study by electrochemical techniques binuclear d^7-d^8 radical species. To avoid the facile ($k \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$) radical recombination reaction exhibited by the $[\text{Rh}_2(\text{bridge})_4]^{3+}$ species,² we have synthesized an axially hindered binuclear Rh(I) d^8-d^8 complex that enables the clean generation of a stable d^7-d^8 binuclear radical for characterization and reaction studies.

$[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2](\text{PF}_6)_2$ (dimen = 1,8-diisocyanomenthane; dppm = bis(diphenylphosphino)methane) is synthesized⁵ in high yield via the modification of a previously reported reaction.⁶⁻⁸ The addition of stoichiometric amounts of 1,8-di-

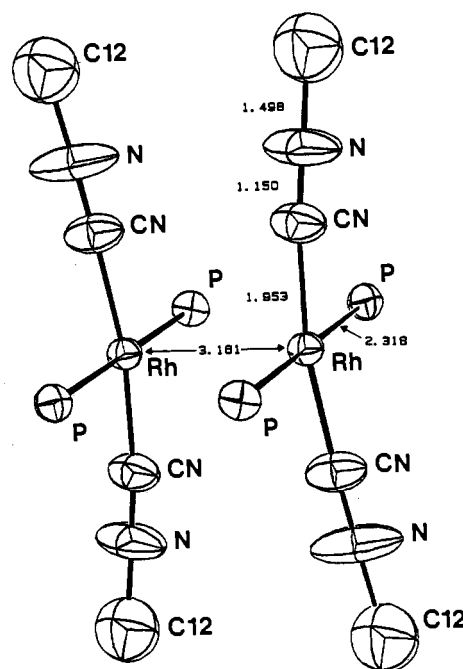


Figure 1. ORTEP drawing of the $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ coordination core. Thermal ellipsoids are at the 50% probability level. Bond angles in degrees: C12-N-CN = 178.8; N-CN-Rh = 173.3; CN-Rh-CN = 168.7; P-Rh-P = 179.6; P-Rh-Rh = 89.8.

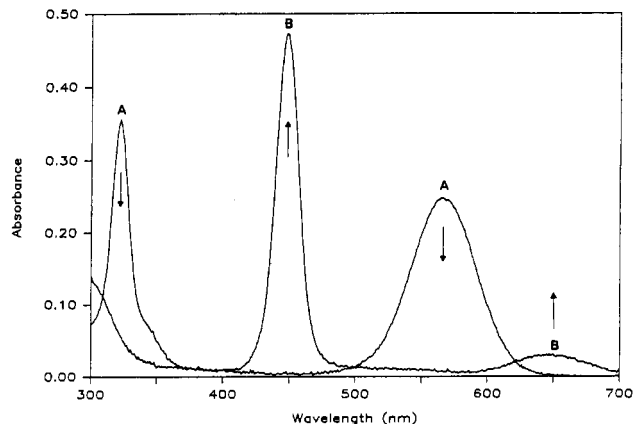


Figure 2. UV-vis spectral changes that result from electrolysis of a 0.7 mM solution of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ at 0.8 V in a transparent thin-layer electrochemical cell. The initial spectrum of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ is labeled A; the final spectrum of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ is labeled B.

isocyanomenthane⁹ to $[\text{Rh}(\text{CO})\text{Cl}(\text{dppm})_2]^{10}$ in methanol allows the isolation of a crystalline product upon addition of NH_4PF_6 .

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- (5) Characterization of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2](\text{PF}_6)_2$ is as follows. ¹H NMR (300 MHz, CD_3CN , 25 °C): dppm phenyl δ 8.165 (m, 4 H), 8.038 (m, 4 H), 7.836 (m, 4 H), 7.652 (m, 4 H), 7.513 (m, 12 H), 7.360 (m, 12 H); dppm methylene δ 4.123 (m, 4 H); dimen methyl δ 0.890 (s, 3 H), 0.634 (s, 3 H), 0.594 (s, 6 H), 0.400 (s, 6 H); dimen methylene and methine protons are observed as multiplets between δ 1.114 and 0.052. Integration confirmed the number of protons in each observed resonance. ³¹P NMR (121.5 MHz, acetone, 25 °C): δ 23.9 (m), vs 85% H_3PO_4 . IR (CH_2Cl_2 solution): $\nu(\text{CN}) = 2132 \text{ cm}^{-1}$. UV-vis (CH_2Cl_2): $\lambda_{\text{max}} = 322 \text{ nm}$, $\epsilon = 2.88 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; $\lambda_{\text{max}} = 565 \text{ nm}$, $\epsilon = 1.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Anal. Calcd: C, 53.99; H, 4.86; N, 3.40. Found: C, 53.80; H, 5.06; N, 3.39.

Table I. Electrochemical Data for $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2](\text{PF}_6)_2$ in CH_2Cl_2 Solutions^a

electrolyte	$E_{3/2}^{0'}$	$E_{p,a} - E_{p,c}^b$	$i_{p,c}/i_{p,a}$	$E_{4/3}^{0'}$	$E_{p,a} - E_{p,c}^b$	$i_{p,c}/i_{p,a}$	D^c
TBAP	+0.700	93	1.0	+1.226	105	1.0	8.67×10^{-6}
TBAH	+0.700	87	1.0	+1.728 ^d			8.30×10^{-6}

^a Measured in volts vs. uncorrected AgCl/Ag reference electrode. Scan rate = 100 mV/s. ^b Measured in mV. ^c D is the diffusion coefficient, measured in cm^2/s by chronocoulometry. A theoretical D value of $6.65 \times 10^{-6} \text{ cm}^2/\text{s}$ is calculated from the Stokes-Einstein equation and structural data. ^d The second oxidation of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2](\text{PF}_6)_2$ is irreversible in $\text{CH}_2\text{Cl}_2/\text{TBAH}$. This value is the anodic peak potential, $E_{p,a}$. No return reduction peak is observed at $v = 100 \text{ mV/s}$ ($i_{p,c} \approx 0$).

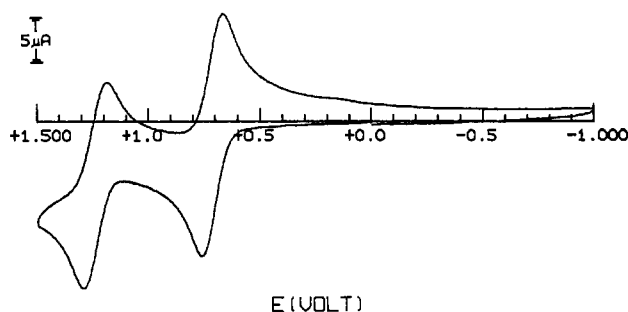


Figure 3. Cyclic voltammogram of a 1.0 mM solution of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ at a glassy-carbon electrode. The scan was initiated in the positive direction at a scan rate of 100 mV/s.

The solid-state structure of this binuclear complex was determined by single-crystal X-ray diffraction techniques¹¹ and is analogous to other face to face d^8-d^8 complexes that have been previously studied.^{12,13} The two diisocyanide and diphosphine ligands are mutually trans, as shown in Figure 1. The Rh-Rh distance of 3.161 (1) Å is typical for Rh(I) binuclear complexes that contain the dppm bridging ligand¹⁴ but is quite atypical for binuclear metal complexes of dimen.^{12,15} For example, $\text{Rh}_2(\text{dimen})_4^{2+}$ exhibits a Rh(I)-Rh(I) distance of 4.479 (2) Å. To accommodate the short Rh(I)-Rh(I) distance, the dimen ligands undergo relatively large bond angle distortions rather than significant bond length distortions. The largest distortion is the reduction of the idealized 180° C-Rh-C angles to $169.7 (3)^\circ$. The electronic structural consequences of these distortions appear relatively unimportant. The UV-vis absorption spectrum (Figure 2a) in room-temperature solutions of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ exhibits the characteristic,^{16,17} low-energy $d_{\pi^*} \rightarrow p_{\pi^*}$ absorption band at 565 nm ($\epsilon = 1.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Additionally, the compound exhibits bright luminescence in fluid solutions at room temperature.

Although the treatment of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ with chlorine in CH_2Cl_2 solutions results in a two-electron oxidative addition reaction¹⁸ analogous to the chlorination of tetrakis(di-

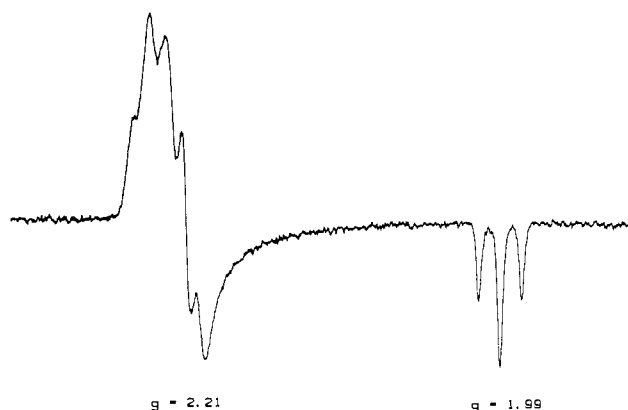


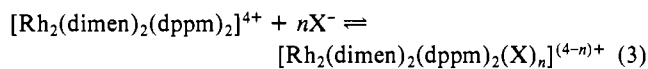
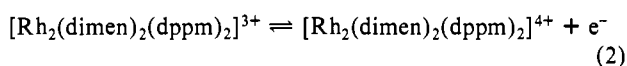
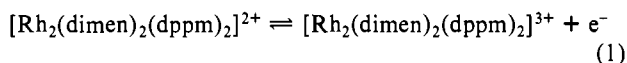
Figure 4. X-band EPR spectrum of a 1.0 mM solution of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ at -165°C .

isocyanide)dirhodium complexes,^{15,19-21} the electrochemical behavior²¹ of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ is simple in comparison to the cases of the tetrakis(diisocyanide)dirhodium complexes previously studied.^{20,22,23} In CH_2Cl_2 solutions, two, one-electron oxidation processes are observed for both PF_6^- and ClO_4^- supporting anions. The one-electron nature of each oxidative process was verified by chronocoulometry and bulk electrolysis studies.²⁴

The cyclic voltammogram of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ (TBAP = tetrabutylammonium perchlorate) is shown in Figure 3, and the electrochemical results are summarized in Table I. The characteristics of the first electrode process are independent of the supporting electrolyte. In contrast, the second oxidation process exhibits some variation in potential and reversibility that is due to complexation equilibria between the 2e oxidized binuclear complex and the supporting anion.¹⁷ The electrochemical behavior of this complex may be summarized by the processes

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- (11) Crystallographic data for $[\text{Rh}(\text{dimen})(\text{dppm})_2](\text{PF}_6)_2$: $M_r = 1644.62$; monoclinic; space group $C2/m$; $a = 16.307 (3) \text{ \AA}$, $b = 18.388 (5) \text{ \AA}$, $c = 14.608 (2) \text{ \AA}$; $\beta = 118.51 (1)^\circ$; $V = 3849 \text{ \AA}^3$; $Z = 2$; $\rho(\text{calcd}) = 1.51 \text{ g/cm}^3$; crystal dimensions $0.20 \times 0.20 \times 0.35 \text{ mm}$; Mo K α radiation, $\lambda = 0.71069 \text{ \AA}$; Enraf-Nonius SPD-CAD4 diffractometer; $R = 0.071$ and $R_w = 0.095$ for 2934 observed reflections with $F_o^2 > 2\sigma(F_o^2)$. An empirical absorption correction was applied. All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs as described previously: Bohling, D. A.; Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1981**, *20*, 194.
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- (18) Characterization of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2\text{Cl}_2](\text{PF}_6)_2$ is as follows. ¹H NMR (300 MHz, CD_3CN , 25°C): dppm phenyl δ 8.255 (m, 4 H), 8.138 (m, 4 H), 8.009 (m, 4 H), 7.905 (m, 4 H), 7.484 (m, 20 H), 7.100 (m, 4 H); dppm methylene δ 4.533 (m, 4 H); dimen methyl δ 1.286 (s, 3 H), 0.958 (s, 6 H), 0.930 (s, 3 H), 0.766 (s, 6 H); dimen methylene and methine protons are observed as multiplets between δ 1.60 and 0.30. Integration confirmed the number of protons in each observed resonance. ³¹P NMR (121.5 MHz, CD_3CN , -20°C): δ 0.400 (m) vs 85% H_3PO_4 . IR (CH_2Cl_2 solution): $\bar{\nu}(\text{CN}) = 2178 \text{ cm}^{-1}$. UV-vis (CH_2Cl_2): $\lambda_{\text{max}} = 402 \text{ nm}$, $\epsilon = 3.00 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; $\lambda_{\text{max}} = 475 \text{ (sh) nm}$, $\epsilon = 3.66 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Anal. Calcd: C, 51.02; H, 4.78; N, 3.26; Cl, 4.14. Found: C, 51.75; H, 4.63; N, 3.23; Cl, 4.89.
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- (24) Electrochemical measurements were performed at a highly polished glassy carbon working electrode at $20 \pm 2^\circ \text{C}$ with a normal three-electrode configuration. Potentials are measured relative to an uncorrected AgCl/Ag reference electrode containing 1.0 M KCl. Ferrocene was used as an internal standard to enable future corrections for the junction potentials. The potential of the $\text{FeCp}_2^+/\text{FeCp}_2$ couple was measured under the various experimental conditions employed: $\text{CH}_2\text{Cl}_2/\text{TBAH}$, $E^{0'} = +0.505 \text{ V}$; $\text{CH}_2\text{Cl}_2/\text{TBAH}$, $E^{0'} = +0.460 \text{ V}$. No IR compensation was used in the electrochemical studies. See: Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.



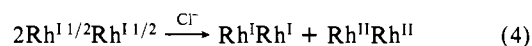
The quasi-reversible nature of the first oxidation process suggested that the electrochemical generation of bulk concentrations of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ might be feasible. Green solutions of the stable d^7-d^8 radical $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ are conveniently generated via bulk electrolysis of $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{2+}$ 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 ($\lambda_{\text{max}} = 448$ nm, $\epsilon = 3.78 \times 10^4$ M⁻¹ cm⁻¹; $\lambda_{\text{max}} = 647$ nm, $\epsilon = 2.50 \times 10^3$ M⁻¹ cm⁻¹) and the transient absorbance spectrum of $[\text{Rh}_2(\text{bridge})_4]^{3+}$ previously obtained² ($\lambda_{\text{max}} = 438$ nm, $\epsilon = 3.45 \times 10^4$ M⁻¹ cm⁻¹; $\lambda_{\text{max}} = 705$ 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 $d_{\sigma_b} \rightarrow d_{\sigma_a}$ transition and the weaker, lower energy feature to a $d_{\sigma_a} \rightarrow p_{\sigma}$ 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 signals²⁸ are observed in the EPR spectrum of the radical species in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ 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 $\text{Rh}_2(\text{CN})_4$ 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 $\bar{\nu}(\text{CN})$ stretching frequency at a relatively high value of 2174 cm⁻¹. The high value for the $\bar{\nu}(\text{CN})$ 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 $[\text{Rh}_2(\text{bridge})_4]^{3+}$ radical that dimerizes at a rate ($k \approx 10^7$ M⁻¹ s⁻¹) approaching the diffusion limit, $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ shows no observable propensity to dimerize on a scale of several days. However, the $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ radical rapidly undergoes disproportionation³⁰ 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 $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ 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:



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 $[\text{Rh}_2(\text{bridge})_4]^{2+}$ through $[\text{Rh}(\text{bridge})_4]^{3+}$ radical disproportionation. This hypothesis is attractive because it is consistent with the low quantum yield observed for hydrogen generation in the $[\text{Rh}_2(\text{bridge})_4]^{6+}$ system under highly acidic conditions. A ligand-induced disproportionation rate for $[\text{Rh}_2(\text{bridge})_4]^{3+}$ that is slow relative 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 ³¹P 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 $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2](\text{PF}_6)_2$ (4 pages). Ordering information is given on any current masthead page.

- (30) The mechanism for the disproportionation reaction 4 may involve the binding of Cl^- to an axial site of the $[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2]^{3+}$ radical as the rate-limiting step. The resulting radical species ($[\text{Rh}_2(\text{dimen})_2(\text{dppm})_2\text{Cl}]^{2+}$) is equivalent to the 19e putative intermediates that have been postulated for photochemical disproportionation reactions of $[\text{CpMo}(\text{CO})_3]_2$. 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.

- (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 minigrad electrode (Buckbee-Mears) sealed between 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 $d_{\sigma_a} \rightarrow p_{\sigma}$ 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 σ_b or σ^* orbital. See: Kawamura, T.; Fukamachi, K.; Sowa, T.; Hayashida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *105*, 364.
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MCPL Evidence for the Transition from Delocalized to Localized Luminescent States of $\text{Ru}(\text{bpy})_3^{2+}$ in Glass-Fluid Media

Sir:

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