# Communications

## High-Temperature HFS for [Ru(bpy⁻)₃]. Verification of the Single Ring Localized Orbital Model

*Sir:*

This communication reports hyperfine structure for the three-electron reduction-product of $RuL_3^{2+}$ type, a result necessary for the clarification of the intramolecular electron hopping for these unique electrochemically generated materials. The unusual spectroscopic and magnetic properties of the reduced materials are rationalized by the concept of the "spatially isolated redox orbital"[1] in which the reduction electrons are sequentially placed into one of three near-degenerate and noncommunicating orbitals each localized on a single diimine chelate ring. Therefore, species as $[Ru(bpy^-)(bpy)_2]^+$ (1), $[Ru(bpy^-)_2bpy]^0$ (2), and $[Ru(bpy^-)_3]^-$ (3) can be obtained. Such a description of the redox orbital predicts that reduced and unreduced ligands are present, and resonance Raman results[2-4] verify this prediction. Moreover a "ligand-based intervalence optical transition" (LBIT) (corresponding to $L^- \rightarrow L$ process) would be expected by analogy to that phenomenon occurring for mixed-valence metal dimer compounds. Such a band is found in the near IR spectrum in the $4000-5000\text{-cm}^{-1}$ region for species 1 and 2.[5,6] The Hush model[7] predicts a thermal activation energy of $\sim 1000 \text{ cm}^{-1}$ for the one-electron-reduction products. Temperature-dependent ESR measurements[8-10] for the one-electron-reduction products exhibit line broadening caused by the electron hopping between rings from which activation energies of $700-1000 \text{ cm}^{-1}$ can be measured for the various complexes. The magnetic properties of the two- and three-electron products are unusual since only $S = \frac{1}{2}$ spectra can be measured in fluid and frozen solution. Optical and resonance Raman spectra for a number of two- and three-electron-reduction products indicate that these materials do have the redox electrons in separate chelate rings maintaining maximum electron correlation. Most recently, criteria have been defined for mixed-ligand complexes, such as $[Ru(bpz^-)(bpy)_2]^+$, that result in measurement of hyperfine splitting[11,12] and, consequently, verification of the





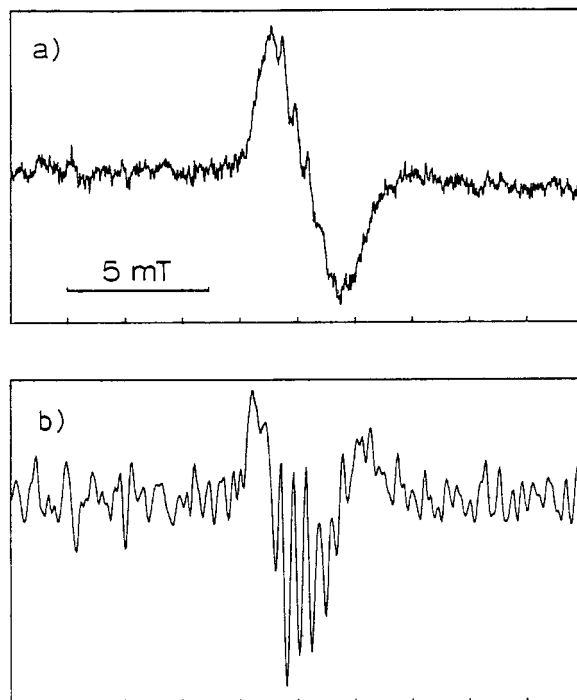**Figure 1.** (a) ESR spectrum and (b) second-derivative spectrum of $[Ru(bpy^-)_3]^-$ in 0.1 M TEAP/DMSO at 348 K.

electron-hopping origin of the line broadening for the tris complexes having one and two electrons. The three-electron tris complexes do not show temperature-dependent line broadening, consistent with the model for which hopping is not permitted for a species as $[Ru(bpy^-)_3]^-$. But to date, no hfs has been observed for any three-electron product, in apparent contradiction to the prediction of the localized orbital model.

To summarize, a number of anomalous ESR results have been identified for these reduction products: (1) Temperature-dependent line broadening with no high-temperature narrowing occurs for the $n = 1$ and $n = 2$ reduction products but not for the $n = 3$ product ($n$ = number of redox electrons). (2) No hyperfine structure can be observed for those reduced species demonstrating temperature-dependent line broadening. (3) No hyperfine structure had been observed for three-electron-reduced (tris) species that do not show temperature-dependent line broadening. (4) Only $S = \frac{1}{2}$ spectra can be measured even for the $n = 2$ and 3 species, implying that the reduced species have diradical ($n = 2$) or triradical character ($n = 3$) or that $D$ is vanishingly small

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for the coupled spin systems.

The first two points of this list can be rationalized by the recognition that hfs splitting cannot be resolved unless the electron hopping between rings is eliminated (or considerably diminished). The results discussed here will remove the third anomaly and provide some insight into point 4.

The preparation of electrolyzed samples under inert-atmosphere conditions has been described previously.[4,9] Spectra were determined with an IBM ESR instrument for the complexes in dimethyl sulfoxide (DMSO) solvent and *N,N*-dimethylformamide (DMF) solvent in some cases. The high temperatures were obtained by using a nitrogen gas variable-temperature apparatus adapted to the IBM cavity system. The voltammetry of the complexes (approximately millimolar concentration) in DMSO is similar to that in DMF, and electrolysis potentials were determined from the voltammograms. The first- and second-derivative ESR spectra for [Ru(bpy⁻)₃]⁻ determined at 75 °C in DMSO are shown in Figure 1. The spectra at 24 °C are anisotropic, similar to that found for other electrolytic solvents near their freezing point. As the temperature is increased the signal becomes isotropic, consistent with rapid tumbling. At temperatures greater than 60 °C and up to 160 °C, the signal-to-noise ratio decreases due to the heating of the cavity and the consequent detuning of the spectrometer. Cycling of the temperature between room temperature and 160 °C does not result in any decomposition in DMSO. While DMF has been the solvent of choice for the prior ESR measurements, DMF does decompose at high temperature and the ESR signal is lost. The ESR spectra of the [Ru(bpz⁻)₃]⁻ species was also obtained at high temperature in DMSO and hfs was measured although the spectra here are not as well resolved as that of [Ru(bpy⁻)₃]⁻. The [Ru(COOetbpy⁻)₃]⁻ complex does not give hfs at high temperature in DMSO because of the very weak signal intensity. The spectra of the two-electron-reduction product [Ru(bpy⁻)₂bpy]⁰ was determined in DMSO and only a broad $S = {}^1/_2$ line could be determined with no hfs observed at any temperature.

The appearance of the hfs at high temperature and the anisotropic spectra just above the solvent melting point indicate that the inability to resolve the hfs is due, in part, to a small amount of $g$ and/or $A$ tensor anisotropy. Further, the absence of high-temperature (60 °C) resolution for [Ru(bpy⁻)₃]⁻ in DMF implies that the DMSO may provide a minor perturbation upon the coupling constant, producing a favorable spectral density. The possibility that the three-electron species is a localized orbital system with a coupling of two spins to give a doublet state remains and could be the origin of some of the loss in ESR intensity for the three-electron relative to the one-electron species. However, for most complexes, the $n = 3$ spectrum is much less intense than the $n = 1$ spectrum rather than having comparable intensity to the spectrum of the one-electron species. Further, the two-electron species are all paramagnetic with intensities comparable to or less than that of the $n = 1$ species.

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### A Novel Route for Macroscale Preparation of the Unsubstituted C₂B₄ Carborane 2,3-Dicarba-*nido*-hexaborane(8)

*Sir:*

Recent dramatic development in the chemistry of C-substituted derivatives of 2,3-dicarba-*nido*-hexaborane(8) has been partly due to availability of improved synthetic procedures for these C-

substituted *nido*-carboranes.[1,2] These new preparative routes are significantly better than the conventional ones[3] in terms of safety, yield, and practicality. However, none of these improved procedures gives the parent C₂B₄ carborane, even in trace quantities. The only available route to the parent carborane has been the method of Onak and co-workers.[3e] This method produces in low yield a complex mixture of *nido*-C₂B₄H₈ and several other unwanted carboranes. Therefore, an investigation of alternative routes for the synthesis of 2,3-dicarba-*nido*-hexaborane(8) is warranted.

We have recently reported that *nido*-2,3-(Me₃Si)₂-2,3-C₂B₄H₆ (I) is produced in multigram quantities (12–13 g/batch; over 73% yield) from a reaction between B₅H₉ and Me₃SiC≡CSiMe₃ at elevated temperature.[2a,b] We have also shown that one of the C(cage)–Si bonds in I could be cleaved effectively to produce *nido*-2-(Me₃Si)-2,3-C₂B₄H₇ (II), in 90% yields.[2c] During the course of our investigation in this area, we sought to examine the reactivity of both the C(cage)–Si bonds in I toward gaseous HCl at elevated temperatures and at different molar ratios of these reactants.

In a procedure[2c] identical with that employed in the preparation of *nido*-2-(Me₃Si)-2,3-C₂B₄H₇ (II), *nido*-carborane I (9.38 g, 42.7 mmol) was allowed to react with pure anhydrous HCl gas (141 mmol) in a molar ratio of 1:3.3 at 160–170 °C for 4 days in a high-vacuum stainless-steel cylinder. This reaction produced II (1.97 g, 13.34 mmol; 31% yield based on I consumed), a mixture of Me₃SiCl and *nido*-2,3-C₂B₄H₈ (III) (9.92 g), and *closo*-C₂B₄H₂Cl₄ (IV) (0.81 g, 3.82 mmol; 8.9% yield based on I consumed), which were collected in traps held at −45, −95, and −196 °C, respectively. A substantial quantity of H₂ gas (19.42 mmol) produced in the reaction was pumped out. Since the parent C₂B₄ carborane (III) is highly miscible in Me₃SiCl, separation of III from Me₃SiCl by vacuum fractionation was unsuccessful. Therefore, a new separation procedure was used by condensing the mixture of Me₃SiCl and III at −196 °C into a Pyrex-glass reactor of 0.5-L capacity that had been previously charged with anhydrous LiAlH₄ (3.95 g, 104.0 mmol) and a magnetic stirring bar. After stirring of this heterogeneous mixture at −78 °C for 12 h and then at room temperature for 36 h, the volatiles were fractionated to collect Me₃SiH (5.11 g, 69.05 mmol) and parent C₂B₄ carborane (III) (0.89 g, 11.71 mmol; 27% yield based on I consumed) in traps held at −196 and −95 °C, respectively. A noncondensable gas, identified as H₂ (22.3 mmol), produced during this reduction process was pumped out. A substantial quantity (0.33 g, 1.34 mmol) of transparent crystals was collected in trap held at −78 °C, and these crystals were identified by spectroscopy as unsolvated (Me₃Si)₃Al.[4] Scheme I represents the reaction pathways during the production of III.

The reaction of II with HCl in a molar ratio of 1:1.5 under similar conditions produced III and IV in 30% and 15% yields, respectively. When the molar ratio of I to HCl was 1:10, under similar conditions the reaction shown in Scheme I produced IV in 91% yield as the sole carborane product. When the molar ratio

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