A ^{1}H NMR Study of Reduced Paramagnetic Tris(2,2'-bipyridine) Complexes of Iron(II), Ruthenium(II), and Osmium(II)

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Abstract: ^{1}H NMR contact shifts were measured for [M(bpy)$_3$]$^-$ and [M(bpy)$_3$]$^+$ (M = Fe(II), Ru(II), and Os(II)) by Fourier transform NMR. From these data, spin density distributions for [M(bpy)$_3$]$^-$ were estimated as follows: $\rho_5 \gg \rho_3 > \rho_4 > \rho_6$ where ρ_6 is negative. The values of spin density for [M(bpy)]$^-$ are smaller than expected from comparison with those by bpy$^-$ and [Ru(bpy)$_3$]$^+$, thus suggesting a complication in magnetic susceptibility for [M(bpy)$_3$]$^-$. Consideration of the line widths of [M(bpy)$_3$]$^+$ indicates that ^{1}H NMR may permit measurement of electron-hopping rate constants for [M(bpy)$_3$]$^+$, [M(bpy)$_3$]^0, and their analogues. Such data can corroborate results from the ESR line broadening caused by the intramolecular electron hopping.

The [Ru(bpy)$_3$]$^{2+}$ complex (bpy = 2,2'-bipyridine) and its analogues have unique optical and electron-transfer properties that permit these materials to act as photosensitizers. Recently our ESR studies[1] provided strong evidence for the spatially isolated orbital model of d^6 transition-metal diimine complexes. Specifically, an $S = ^1/_2$, $g \sim 2.00$ spectrum is observed for one-, two-, and three-electron reduction products of a number of Ru(L$_3$)$^{2+}$ complexes (L = π electron diimine ligand as bpy). These data indicate that the reduced complexes are best described as ligand localized radical species, i.e., that the metal is best approximated as a diamagnetic Ru(II). Moreover, the absence of any evidence for $S = 1$ spectra for the two-electron reduced species and $S = ^3/_2$ spectra for the three-electron product implies that the unpaired electrons do not couple, i.e., that to a good approximation, the electrons exist in spatially isolated orbitals localized in individual π ligands. The additional occurrence of a temperature dependent line broadening for the one- and two-electron reduced species but not the three-electron species can be rationalized as electron hopping from, for example, a bpy$^-$ ligand to a bpy ligand. The activation energy calculated from the ESR line broadening gives, for the one-electron species, a value that, with the Hush theory for mixed valence state metal dimers, enables estimation of an optical energy for the ligand-based electron-transfer process. Heath first measured[2a] such a ligand-based intervalence transition (LBIT) for [Ru(bpy)$_3$]$^+$ and [Ru(bpy)$_3$]^0, and we have measured this band[2b] for the one- and two-electron species (the three-electron product should not and does not exhibit this band). Moreover we have recently measured resonance Raman spectra[3] for these reduced tris complexes and demonstrated that the data are best interpreted as indicating the presence of distinct bpy^{1-} and bpy ligand forms for the reduction products of [Ru(bpy)$_3$]$^{2+}$. All of these redox orbital data are consistent with photoselection[4] and resonance Raman[5] data for the lowest excited state of the parent complex which also indicates localization of the optical orbital on a single ligand.

Electron spin density data for [Ru(bpy)$_3$]$^{n+}$ can be useful in designing a suitable photosensitizer for the charge separation required in solar energy conversion by varying substituents or redox functional groups in the bpy moiety. These data can also be crucial in determining the validity of molecular orbital (MO) calculations.

Unfortunately, spin density data have not been reported for these metal complexes since ESR spectra of reduced tris(bpy) complexes of Fe(II), Ru(II), Os(II), and Ir(III) typically give only one very broad line and thus do not give useful hyperfine structure, owing to their rapid electronic relaxation time. However, these relaxation conditions can be advantageous for the measurement of ^{1}H NMR contact shifts for paramagnetic complexes in solution[5] when the following is observed:

$$T_{re}^{-1} \gg (\gamma_e/2\pi)a_N \text{ and/or } T_{ex}^{-1} \gg (\gamma_e/2\pi)a_N \qquad (1)$$

where T_{re} is the electronic relaxation time, T_{ex} the electronic exchange time, γ_e the gyromagnetic ratio of the electron, and a_N the hyperfine coupling constant. For the one- and two-electron reduced complexes, the relaxation time T_1 is determined by an intramolecular electron-hopping process. For the three-electron reduction product, the absence of hyperfine structure is less readily understood but may reflect electron exchange (T_e).

While typical *paramagnetic* transition-metal complexes (unpaired electron residing primarily in the metal d orbitals) may have both dipolar and Fermi contact shift contributions[6] to the experimental NMR contact shift, the ESR and NMR data available for these complexes suggest that the Fermi contact shift dominates any dipolar shift contribution consistent with the ligand localized character of these materials. The Fermi contact shift (δ_c) is generally given by eq 2,[6] where S is the total spin quantum

$$\delta_c = \Delta H/H = -a_N g_e \beta_e S(S+1) \gamma_e \gamma_N 3kT \qquad (2)$$

number, and other symbols have their usual significance. In the present paper, we have estimated spin density distributions of singly and triply reduced tris(bpy) complexes of Fe(II), Ru(II), and Os(II) from ^{1}H NMR contact shift measurements.

Experimental Section

Materials. Dimethyl-d_6 sulfoxide (99.5 atom %), Me$_2$SO-d_6, and acetonitrile-d_3 (99.7 atom %), AN-d_3, were obtained from Merck Sharp and Dohme (Canada Limited). The Me$_2$SO-d_6 was dried over molecular sieves (Alfa, Linde AW 500). The degassed Me$_2$SO-d_6 was mixed with sodium anthracenide and allowed to stand for several days Me$_2$SO-d_6 appears to react with sodium anthracenide very slowly). The Me$_2$SO-d_6 was vacuum-distilled into a Schlenk tube with sample and supporting electrolyte. The AN-d_3 was vacuum-distilled over P$_2$O$_5$. Tetraethylammonium perchlorate (TEAP) was supplied by Eastman Kodak, recrystallized from water four times and from methanol once, and vacuum dried. The Me$_2$SO-d_6 and AN-d_3 solutions were treated under a nitrogen atmosphere and used after vacuum distillation. [Ru(bpy)$_3$](ClO$_4$)$_2$[7] and

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Table I. ^{1}H NMR Spectral Data for Parent Complexes[a]

complex	solvent	chemical shift vs. Me$_4$Si (ppm)			
		H(3,3')	H(4,4')	H(5,5')	H(6,6')
[Ru(bpy)$_3$]$^{2+}$	Me$_2$SO-d_6	8.78 (d, 8.8)	8.14 (t, 8.0)	7.51 (t, 6.0)	7.72 (d, 5.0)
[Ru(4,4'-dmbpy)$_3$]$^{2+}$	Me$_2$SO-d_6	8.67 (s)	[3.21]^{b,c} (s)	7.32 (d, 6.3)	7.52 (d, 5.8)
[Ru(5,5'-dmbpy)$_3$]$^{2+}$	Me$_2$SO-d_6	8.64 (d, 8.5)	7.95 (d, 8.5)	[2.18]^b (s)	7.41 (s)
[Os(bpy)$_3$]$^{2+}$	AN-d_3	8.48 (d, 8.5)	7.85 (t, 7.8)	7.29 (t, 6.8)	7.63 (d, 6.3)
[Fe(bpy)$_3$]$^{2+}$	AN-d_3	8.51 (d, 8.3)	8.09 (m)	7.4 (m)	7.4 (m)

[a] Values in parentheses are apparent coupling constants in hertz. (s, singlet; d, doublet; t, triplet; m, multiplet.) [b] Chemical shifts of methyl protons. [c] Observed by intense signals of TEAP in this region.

[Fe(bpy)$_3$](ClO$_4$)$_2$[8] were prepared by literature methods and recrystallized from methanol and acetone, respectively. [Os(bpy)$_2$](ClO$_4$)$_2$ was received from Robert Donohoe of this department. [Ru(4,4'-dmbpy)$_3$](ClO$_4$)$_2$ and [Ru(5,5'-dmbpy)$_3$](ClO$_4$)$_2$ (4,4'-dmbpy = 4,4'-dimethyl-2,2'-bipyridine; 5,5'-dmbpy = 5,5'-dimethyl-2,2'-bipyridine) were prepared by the method of Creutz et al. except that RuCl$_3$·xH$_2$O was used in place of K$_2$RuCl$_5$(H$_2$O).[9] Purity of these complexes was checked by cyclic voltammetry in dry dimethylformamide at about −54 °C.

Electrolysis. The two compartments in the electrolysis cell were separated by a medium porosity glass frit. A small platinum wire (for cyclic voltammetry), a platinum gauze (for electrolysis), and silver wire quasi-reference electrode were placed in the working compartment; a platinum gauze counter electrode was placed in the counter compartment and further separated by another glass frit. The quasi-reference electrode was isolated from the working compartment by a Vycor glass plug; its open circuit potential was quite stable. Before and after controlled potential electrolysis, cyclic voltammetry was used to check electrode potentials and to verify the stability of reduced complexes. The very low solubility of the doubly reduced complexes [M(bpy)$_3$]^0 was a significant problem. In AN-d_3 [M(bpy)$_3$]^0 precipitates immediately, and in Me$_2$SO-d_6, 30 min after electrolysis, the sample solution was almost colorless. Precipitated [Ru(bpy)$_3$]^0 did not give any ^{1}H NMR signal under the same conditions. The concentration of sample solution was 3–6 mM in Me$_2$SO-d_6 and 2 mM in AN-d_3, and the supernatant solutions of triply reduced complexes were used for NMR measurement. From the cyclic voltammetry results, most of the [Ru(bpy)$_3$]$^{2+}$ was recovered as [Ru(bpy)$_3$]$^-$ in Me$_2$SO-d_6, but this was not possible in AN-d_3. Due to the low solubility (or instability), NMR measurements for [Ru(5,5'-dmbpy)$_3$]$^-$ and [Fe(bpy)$_3$]$^-$ were unsuccessful. The NMR spectrum for [Ru(4,4'-dmbpy)$_3$]$^+$ could not be determined, probably due to limited solubility.

^{1}H NMR **Measurement.** All Fourier transform NMR measurements were performed on a Bruker WM 250 spectrometer. The number of scans was typically 100 with a pulse delay time of 3 s. All ^{1}H NMR chemical shift values were referenced to Me$_4$Si.

Results and Discussion

[M(bpy)$_3$]$^{2+}$. Table I summarizes ^{1}H NMR spectral data for the parent complexes, [Ru(bpy)$_3$]$^{2+}$, [Ru(4,4'-dmbpy)$_3$]$^{2+}$, [Ru(5,5'-dmbpy)$_3$]$^{2+}$, [Os(bpy)$_3$]$^{2+}$, and [Fe(bpy)$_3$]$^{2+}$. The abbreviations s, d, t, and m denote the singlet, doublet, pseudo-triplet, and multiplet, respectively. Assignments were made by examination of the splitting patterns of the two methyl derivatives of [Ru(bpy)$_3$]$^{2+}$. There are small differences in chemical shifts among Fe(II), Ru(II), and Os(II) complexes, but these are not rationalized at present.

[M(bpy)$_3$]$^-$. Figure 1 shows a typical ^{1}H NMR spectrum of [Ru(bpy)$_3$]$^-$, the three-electron reductant, in Me$_2$SO-d_6 with TEAP at 23 °C. The very intense signals at ~0 ppm are also seen in a blank solution with supporting electrolyte and thus are signals for the electrolyte. The other four peaks, one at low field and three at high field, correspond to the four ring protons of bpy; H(3,3'), H(4,4'), H(5,5'), and H(6,6'). The line widths of these
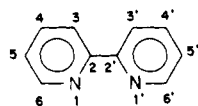
signals increase rapidly with the absolute value of contact shift, $|\delta_c|$. The integrals of these signals are equal within experimental
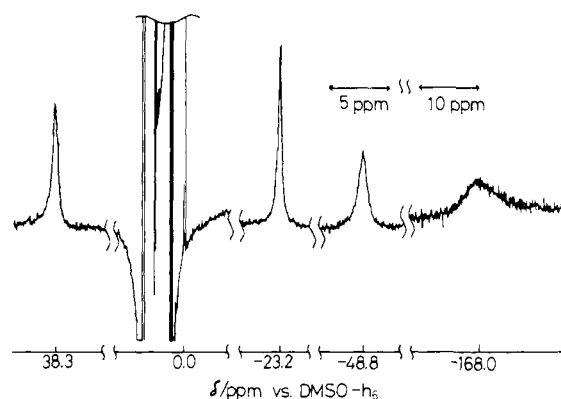

Figure 1. A typical ^{1}H NMR spectrum of [Ru(bpy)$_3$]$^-$ in Me$_2$SO-d_6 at 23 °C. The concentration of [Ru(bpy)$_3$]$^-$ is 5 mM and that of TEAP is 50 mM.
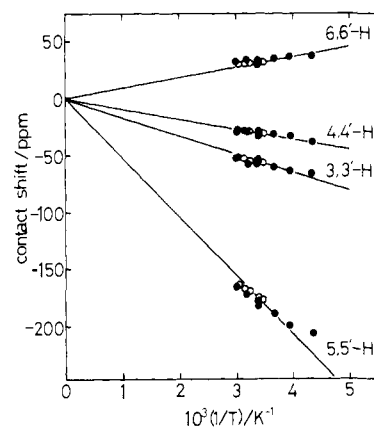
Figure 2. Curie plots for [Ru(bpy)$_3$]$^-$ in AN-d_3 (●) and in Me$_2$SO-d_6 (○). The concentration of [Ru(bpy)$_3$]$^-$ in Me$_2$SO-d_6 is 5 mM and that in AN-d_3 is less than 2 mM.

error (±20%). Changing in the pulse delay time from 3 to 10 s did not produce any change in the intensity ratio.

Assignments. The ESR studies and MO calculations on bpy by Konig[10] and Kaim[11] and our recent MNDO MO study[12] indicate that the electron density on the 5 and 5' positions is largest, and that on the 6 and 6' positions is smallest. Substituents on 5 and 5' positions are more effective in altering the first reduction potentials of bpy and [Ru(bpy)$_3$]$^{2+}$ than those on 4 and 4' positions.[13] These theoretical and experimental data enable assignment of the peak at the highest field as H(5,5') and the lowfield peak as H(6,6'). To complete the assignments, [Ru(4,4'-dmbpy)$_3$]$^-$ was examined. This complex gives two low-field peaks (18, 38 ppm) and two high-field peaks (−75, −186 ppm). Methyl substitution has a minimal effect upon proton hyperfine

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Table II. ^{1}H NMR Contact Shifts for Reduced Tris(bpy) Complexes of Fe(II), Ru(II), and Os(II) at 23 °C^a

			contact shift in ppm			
no.	complex	solvent	H(6,6′)	H(4,4′)	H(3,3′)	H(5,5′)
1	[Ru(bpy)$_3$]$^-$	Me$_2$SO-d_6	30.53 (140)	−31.34 (95)	−57.58 (210)	−175.5 (∼1800)
2	[Ru(bpy)$_3$]$^{-b}$	Me$_2$SO-d_6	29.60 (140)	−35.09 (190)	−55.73 (310)	−172.5
3	[Ru(bpy)$_3$]$^-$	AN-d_3	31.13 (140)	−35.29 (120)	−58.2 (280)	−182
4	[Ru(bpy)$_3$]$^{-c}$	AN-d_3	35.18 (260)	−40.74 (330)	−67.28 (520)	−208
5	[Ru(4,4′-dmbpy)$_3$]$^-$	Me$_2$SO-d_6	18.35 (130)	[37.54]^d (210)	−74.93 (530)	−185.9 (∼2500)
6	[Os(bpy)$_3$]$^-$	AN-d_3	20.17 (50)	−16.20 (25)	−37.96 (110)	−107.7 (750)
7	[Ru(bpy)$_3$]$^+$	Me$_2$SO-d_6	16.18 (1500)			
8	[Ru(bpy)$_3$]$^+$	AN-d_3	15.58 (1000)	−16^e		
9	[Ru(5,5′-dmbpy)$_3$]$^+$	Me$_2$SO-d_6	10.09 (750)	−7^e	−22^e	
10	[Os(bpy)$_3$]$^+$	AN-d_3	8.14 (120)	−13.9^e	−36^e	
11	[Fe(bpy)$_3$]$^+$	AN-d_3	12			

^{a} Values in parentheses are half-maximum line widths in hertz. ^{b} Sample solution in the first row was diluted by a factor of 4 times of pure solvent. ^{c} At −39 °C. ^{d} Contact shift of methyl protons. ^{e} Vs. Me$_4$Si.

coupling constants of bpy$^-$,[10] and similarly does not alter significantly the first reduction half-wave potentials of bpy and [Ru(bpy)$_3$]$^{2+}$. The integral of the peak at 18 ppm relative to that at 38 ppm approaches a one to three ratio (1:3) with an increase in the pulse delay time from 3 to 10 s, indicating that the methyl protons have rather long T_1 values. Consequently, the following assignments were obtained:

$$\delta_c(6,6′) > \delta_c(4,4′) > \delta_c(3,3′) > \delta_c(5,5′)$$

The signs of $\delta_c(6,6′)$ and $\delta_c(CH_3)$ are positive. In Table II are listed contact shifts (δ_c) and line widths for [M(bpy)$_3$]$^-$, together with data for [M(bpy)$_3$]$^+$.

Origin of Contact Shift. The temperature dependence of the chemical shifts enables identification of a contact shift process. In Figure 2 the Curie plots are shown for [Ru(bpy)$_3$]$^-$. Although a slight deviation of these plots from linearity may be an indication of some complication by thermal equilibrium as shown in the cases of organic polyradicals,[14] the shifts of the peaks are essentially linear with the reciprocal of temperature consistent with a Fermi contact interaction. Moreover, the observation of a sign reversal for the contact shift when the 4 position proton is replaced by the CH$_3$ group has frequently been used as a diagnostic for a dominant contact shift.[6a] The absence of dipolar coupling terms in the ESR and the very small g anisotropy for the Ru complexes are also consistent with a contact shift mechanism for the NMR shift. Finally the NMR line width is proportional to the square of the shift as predicted for a Fermi contact interaction (see Line Width). From these data, proton hyperfine coupling constants (a), and further the spin density (ρ), can be calculated by eq 2. The corresponding values for other complexes were calculated from the contact shifts at room temperature (23 °C). In Table III, proton hyperfine coupling constants and spin densities obtained from McConnell's relation ($a = Q\rho$; $Q = -22.5$ G for ring proton, and $Q = 27$ for methyl proton attached to ring) are summarized. Table III also includes data for free bpy$^-$ from ESR measurements.[10] The relative magnitudes and ratios of the spin densities calculated from the McConnell equation are consistent with those predicted by the MNDO calculation (done for the free ligand). This supports the assumption that these paramagnetic species behave as π-electron radical with little d-orbital participation and there is a reasonable first approximation to the situation.

Line Width. The widths of NMR lines for organic radicals such as biphenyl negative ion have been accounted for by intramolecular interactions.[14]

$$T_2^{-1} = (T_2^{-1})_{FC} + (T_2^{-1})_D + (T_2^{-1})_{other} \tag{3}$$

$$(T_2^{-1})_{FC} = (1/3)a_i^2\gamma_e^2 S(S+1)[t_e + t_e(1 + \omega_e^2 t_e^2)^{-1}] \tag{4}$$

$$(T_2^{-1})_D =$$
$$(1/15)\rho^2\gamma_e^2\gamma_N^2 h^2(1/r^6)S(S+1)[7t_d + 13t_d(1 + \omega_e^2 t_d^2)^{-1}] \tag{5}$$

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Table III. Proton Hyperfine Coupling Constants (a) in Gauss and Spin Densities (ρ) of Reduced Tris(bpy) Complexes of Fe(II), Ru(II), and Os(II)^a

		position			
complex		6,6′	4,4′	3,3′	5,5′
[Ru(bpy)$_3$]$^-$	a/G	0.408	−0.419	−0.770	−2.347
	ρ	−0.0181	0.0186	0.0342	0.1043
[Ru(4,4′-dmbpy)$_3$]$^-$	a/G	0.245	−0.502	−1.002	−2.486
	ρ	−0.0109	0.0184^b	0.00445	0.1105
[Os(bpy)$_3$]$^-$	a/G	0.270	−0.217	−0.508	−1.440
	ρ	−0.0120	0.0096	0.0226	0.064
[Ru(bpy)$_3$]$^+$	a/G	0.649	(0.666)	(1.225)	(3.733)
	ρ				
[Ru(5,5′-dmbpy)$_3$]$^+$	a/G	0.438			
	ρ				
[Os(bpy)$_3$]$^+$	a/G	0.405			
	ρ				
[Fe(bpy)$_3$]$^+$	a/G	0.48			
	ρ				
bpy^{-c}	a/G	0.57	0.71	1.66	4.91
	ρ				

^{a} Observed values were multiplied by a factor of three for singly reduced complexes. ^{b} Obtained from McConnell's relation $a = Q\rho$ (where $Q = 27.3$ for methyl protons of 4-picoline radical anion [ref 16]. ^{c} Reference 10.
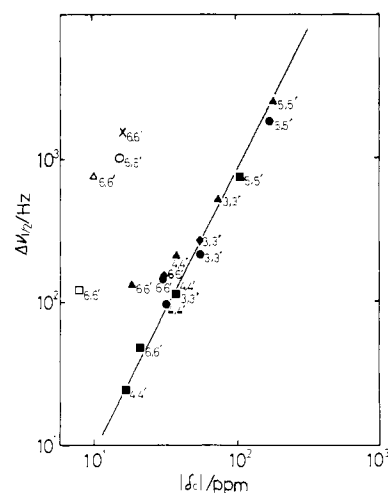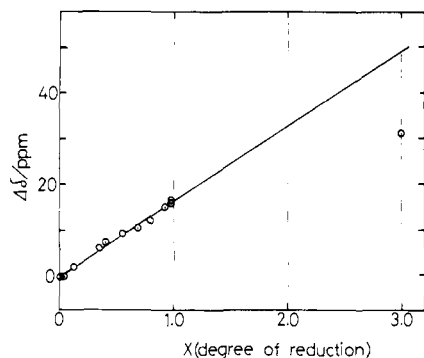

Figure 3. The log $\Delta\nu_{1/2}$ vs. log $|\delta_c|$ plot for (●) [Ru(bpy)$_3$]$^-$ in Me$_2$SO-d_6; (♦) [Ru(bpy)$_3$]$^-$ in AN-d_3; (▲) [Ru(4,4′-dmbpy)$_3$]$^-$ in Me$_2$SO-d_6; (■) [Os(bpy)$_3$]$^-$ in AN-d_3; (×) [Ru(bpy)$_3$]$^+$ in Me$_2$SO-d_6; (○) [Ru(bpy)$_3$]$^+$ in AN-d_3; (△) [Ru(5,5′-dmbpy)$_3$]$^+$ in Me$_2$SO-d_6; (□) [Os(bpy)$_3$]$^+$ in AN-d_3 at 23 °C. ▲$_{4,4′}$ is the data for methyl protons. $\Delta\nu_{1/2}$ is the line width at half-maximum intensity, and $|\delta_c|$ is the absolute value of contact shift. Numerals denote the position of protons.

In these equations, t_e is the electron correlation time, t_d is the dipolar correlation time defined by $t_d^{-1} = t_e^{-1} + t_r^{-1}$, where t_r is the rotational correlation time, and the FC and D denote the Fermi contact and dipolar interactions, respectively. From eq 3 and 4,

Figure 4. The change in chemical shift of 6,6′-H ($\Delta\delta$) vs. the degree of reduction (X) for a Me_2SO-d_6 solution of 5 mM $[Ru(bpy)_3]^{2+}$ with 50 mM TEAP at 23 °C.

(T_2^{-1}) is proportional to a_i^2, or δ_c^2 at constant temperature. In Figure 3, the logs of the line widths at half-maximum intensity (log $\Delta\nu_{1/2}$) are plotted against $\log|\sigma_c|$ for $[Ru(bpy)_3]^-$, $[Ru(4,4'-dmbpy)_3]^-$, and $[Os(bpy)_3]^-$. This straight line with the theoretical slope, 2, means that the H(3,3′), H(4,4′), and H(5,5′) of the three complexes exhibit the same line-broadening mechanism, while that of the 6 and 6′ position protons are distinct. This behavior of the H(6,6′) protons and the negative spin density for H(6,6′) are analogous to those observed for the biphenyl meta protons.[14] From the plot in Figure 3 and eq 2 and 4, t_e is calculated as 1.1×10^{-9} s at room temperature assuming that the first term in eq 3 is predominant. Such a value is consistent with the observations of broad ESR lines at these temperatures. The line widths of the four peaks in Me_2SO-d_6 are temperature independent, indicating that the main electron relaxation process for $[M(bpy)_3]^-$ is probably intramolecular electron spin–spin exchange or electron dipole–dipole interaction with a very small activation energy. The latter mechanism has been used to explain the difficulty of ESR measurement for a multispin organic system.[15]

Contact Shift and Line Width of $[M(bpy)_3]^+$. In Table II contact shift data are summarized for $[M(bpy)_3]^+$, the one-electron reductant. Each complex shows one rather broad peak at low field which corresponds to H(6,6′) and one or two very broad peaks at high field. From our ESR study[1] for these and similar complexes, the contact shift of $[M(bpy)_3]^+$ is expected to be one-third of that for $[M(bpy)_3]^-$ and the line width of the $[M(bpy)_3]^+$ peak should result from an intramolecular electron-hopping process among the three ligands.

These line widths for $[Ru(bpy)_3]^+$, $[Ru(5,5'-dmbpy)_3]^+$, and $[Os(bpy)_3]^+$ (Figure 3) demonstrate that the line broadening mechanism for the singly reduced complexes is different from that of their triply reduced counterparts. The line widths of $[Ru(bpy)_3]^+$ and $[Ru(5,5'-dmbpy)_3]^+$ decreased with increasing temperature while, as pointed out earlier, those for the three-electron complexes do not change with temperature. If the predominant broadening mechanism is "electron-hopping", eq 4 can explain these line widths by replacing a_i by $^1/_3a_i$ and t_e by the reciprocal of the electron-hopping rate derived from ESR data. Furthermore, if the contribution from *intermolecular* electron self-exchange due to incomplete reduction is negligible, then these preliminary data give virtually the same activation energy and preexponential factor as our ESR data.[1] This suggests that the

broadening of NMR proton signals of $[M(bpy)_3]^+$ is primarily determined by electron hopping and thus permits the study of this process for molecules whose kinetics could not be determined by ESR since the lines were broadened excessively.[17]

From the ESR data and the simple model, the electron spin density of $[Ru(bpy)_3]^-$ (three-electron product) is predicted to be three times that of the $[Ru(bpy)_3]^+$ (one-electron product) in NMR measurements at high temperature. However, the contact shift of H(6,6′) of $[Ru(bpy)_3]^-$ is not three times that of the $[Ru(bpy)_3]^+$. In Figure 4 the contact shifts of H(6,6′) are plotted vs. the degree of reduction of $[Ru(bpy)_3]^{2+}$ demonstrating this point. The dipolar shift resulting from more than one unpaired electron was ignored in organic polyradicals;[14] however, H(6,6′) in $[Ru(bpy)_3]^-$ may be subjected to such interaction by the unpaired electrons of the other bpy⁻ rings in our case as these H(6,6′) are very near to the other ligands. The other protons may be much less affected since the dipolar interaction decreases rapidly with the distance; but, unfortunately, the spectra for the one-electron product does not permit comparison of spin densities for other positions.

Alternatively, the formation of two doublet ground states with a thermally accessible quartet excited state for the three-electron system of $[M(bpy)_3]^-$ would result if any spin–spin interaction exists for this species. Such a model has been used to explain the temperature dependence of contact shift for organic biradicals.[14] This model would allow $[M(bpy)_3]^-$ to undergo rapid interligand electron spin–spin exchange, so that rather narrow NMR signals would occur (eq 3). This would also result in smaller contact shifts than predicted by the straight line Curie plot as temperature decreases. At present, no evidence for this latter model exists since magnetic suceptibilities cannot be measured for these dilute radical solutions with standard techniques. However, such a spin paired model requires a low-lying ^2E state, and thus any large contribution is unlikely since neither the ESR or the resonance Raman give any indication of degenerate state behavior. The alternative ordering with a quartet ground state, although better able to rationalize the occurrence of room temperature ESR, is not consistent with the absence of additional Δm_s = transitions or the absence of any Δm_s = 2 transitions in the half-field region. Less direct evidence is the fact that the two-electron reduction product does give a solution ESR spectrum with identical g factor to that of the one- and three-electron reduction product and that no evidence for spin–spin coupling is observed in this ESR (nor in other types of spectra) of this species. If the three-electron species could produce a quartet ground-state species, implying the near degeneracy of a and e *orbitals*, then an E ground state would logically be expected for the two-electron system, a state for which no solution ESR could be measured contrary to observation. Thus, with the currently available data, no magnetic coupling between the unpaired electrons is apparent (i.e., the unpaired electrons exist in spatially isolated orbitals; degenerate orbitals that are in close proximity but with minimal interaction). Experiments to understand the origin of this localization are in progress.

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