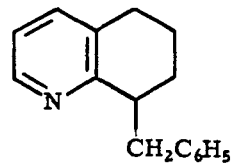
Table I. Diastereotopic Splittings in ^{15}N NMR Spectra of Racemic 8-Benzyl-5,6,7,8-tetrahydroquinoline (**1**) in the Presence of Optically Active Proton Donors at 26.5 °C

optically active compd	concn, mol %	concn of **1**, mol %	solvent	av ^{15}N shift, ppm[a]	assocn shift, ppm[b]	diastereotopic shift, Hz
R-(−)-mandelic acid	8.7	23.7	$O(C_2H_4)_2O$	70.5	(~35)	6.6
	8.0	13.5	C_2H_5OH	92.7	(~40)	5.0
	4.1	10.4	CH_2Cl_2	81.6	51.4	12.0
	6.7	16.0	CH_3CN	81.7	(~50)	0
(*S*)-(+)-lactic acid	23.0	23.0	$O(C_2H_4)_2O$	82.4[c]	23.6[c]	3.0[c]
(*R*)-(+)-$CF_3C(OCH_3)(C_6H_5)CO_2H$	2.2	10.3	CH_2Cl_2	75.6	(~67)	12.5
(*R*)-(−)-$CF_3CH(OH)C_6H_5$[d]	17.2	17.0	CH_2Cl_2	72.4	11.0	0
β-cyclodextrin hydrate	1.0	8.6	$(CH_3)_2SO$	61.4	(~10)	3.8

[a] Chemical shifts are given in parts per million upfield from external 1 M $H^{15}NO_3$ dissolved in D_2O and taken at 18.25 MHz in 25-mm tubes with a Bruker WH-180 spectrometer. [b] For a 1:1 mole ratio of **1** to complexing agent; values extrapolated to the 1:1 ratio from smaller ratios are enclosed in parentheses. [c] Measured at 15 °C. [d] Optical purity 25%.

have been done with (*R*)-(−)-mandelic acid and, as will be seen from the data in Table I, the magnitudes of the ^{15}N shift differences with the enantiomers of **1** and (*R*)-(−)-mandelic acid



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are quite sensitive to the nature of the solvent and, in general, the less polar solvents are associated with larger differential shifts. For most experiments, the proportions of proton donor to **1** were kept <1:1 with the hope of maximizing the shift differences through taking advantage of possible differences in the association equilibrium constants. In most cases, however, the degree of NMR nonequivalence of the nitrogens increased when more proton donor was added. The splittings were also found to increase with decreasing temperature. When (*R*)(+)-3,3,3-trifluoro-2-methoxy-2-phenylpropionic acid (**2**) is the complexing agent,[6] a shift difference between the nitrogens of the enantiomers in dichloromethane of 0.70 ppm was observed, and this difference, as expected, disappeared when racemic **2** was used in place of (*R*)-(+)-**2** and the average surroundings of each enantiomer of **1** become identical.

The NMR nonequivalence of the nitrogens of the enantiomers in the presence of β-cyclodextrin hydrate in dimethyl sulfoxide solution is interesting because dimethyl sulfoxide is an excellent hydrogen-bond acceptor and would be expected to saturate the hydrogen-bond-donating powers of the β-cyclodextrin. Perhaps with this combination there is some tendency for preferential insertion of the phenyl ring of one of the enantiomers of **1** into the chiral void of the β-cyclodextrin.

The origin(s) of the shift differences produced by complexing optically active acids with **1** is uncertain. The ^1H NMR of the $>CHCH_2C_6H_5$ moiety of **1** indicates a strong preference for one rotational conformation at the C-8–C-9 bond which, from inspection of models, almost certainly has the benzyl group opposite to the pyridine ring.[7] With a carboxylic acid having a chiral center at the α carbon, the diastereomeric centers would be rather far apart in a hydrogen-bonded complex. Nonetheless, if the benzyl group is in essentially a single conformation, there will be a substantial molecular dissymmetry extending away from the chiral center. The total change of 23.6–67 ppm in ^{15}N NMR shift when **1** is complexed with carboxylic acids (see Table I) is pretty much in the range expected for hydrogen bonding to pyridine,[3,8] and probably represents only a small degree of actual proton transfer and ion-pair formation.

Further experiments are underway to determine the scope of this kind of chiral recognition and its possible applicability to the determination of absolute configurations of pyridine bases or proton donors.

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Electron Nuclear Double Resonance of Ferric Cytochrome $P450_{CAM}$

Sir:

We have used electron nuclear double resonance (ENDOR) to probe the heme environs of cytochrome $P450_{CAM}$, isolated from the prokaryote *Pseudomonas putida*. We studied the native, substrate-free, low-spin ferric m^o and the high-spin ferric component of the enzyme-substrate complex, m^{os}. The ENDOR of the low-spin m^o form showed at least one strongly coupled, exchangeable proton attached to an axial ligand of the heme iron, in good agreement with the interpretation of previous proton relaxation studies.[1] The high-spin m^{os} showed no evidence for histidine or water ligation and indicated five coordination of the heme iron.

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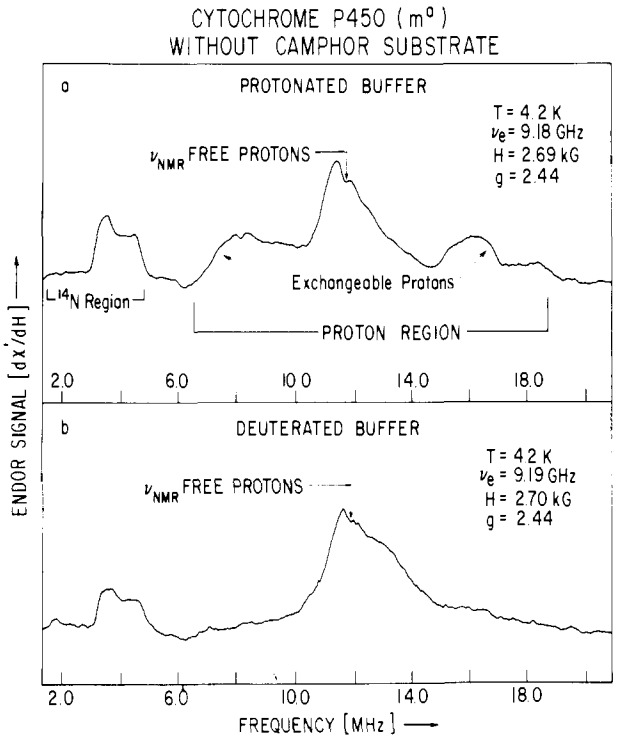

Figure 1. ENDOR spectra of the cytochrome $P450_{CAM}$ m^o in (a) protonated vs. (b) deuterated buffer. The spectra show evidence for an exchangeable proton with total hyperfine coupling of 8–9 MHz. The cytochrome $P450_{CAM}$ heme concentration was 0.7 mM in a buffer (H or D) of 50 mM potassium phosphate, pH 6.8, containing 100 mM KCl. The value of ν_{NMR} for each spectrum is ~11.5 MHz, and each spectrum required ~1 h of signal averaging.

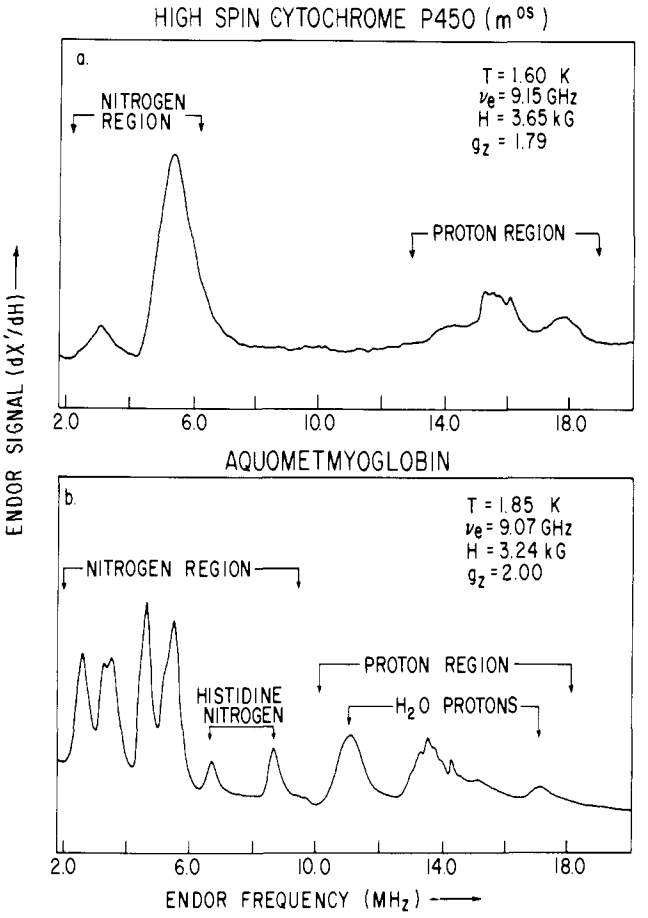

Figure 2. ENDOR spectra in the 1–20-MHz region of (a) high-spin ferric (camphor-bound) m^{os} and (b) high-spin ferric aquometmyoglobin. Aquometmyoglobin was ~5 mM in heme in 1:1 glycerol–phosphate buffer (pH 6.8, 50 mM); essentially identical results were obtained from aquometmyoglobin in the absence of glycerol. Cytochrome $P450_{CAM}$ heme concentration was 1.3 mM in 50 mM potassium phosphate buffer, pH 6.8, containing 100 mM KCl and 100 μM D-(+)-camphor. Values of ν_{NMR} were ~13.8 MHz for myoglobin and 15.5 MHz for the m^{os}. Signal averaging took ~1.5 h for m^{os} and ~0.5 h for myoglobin.

Cytochrome $P450_{CAM}$,[2] a soluble heme protein that catalyzes the 5-*exo*-methylene hydroxylation of the substrate D-(+)-camphor, has served as a biological model for the ubiquitous P450 cytochromes. Isolated in quantity[3] and in three crystalline forms,[4] cytochrome $P450_{CAM}$ has been subjected extensively to chemical and physical probes of the heme-iron active site.[5] These investigations have provided quantitative structural and mechanistic parameters which serve to characterize the broad class of mammalian P450 analogues.[6]

The axial ligation at the heme-iron active site of both the m^o and m^{os} forms of cytochrome $P450_{CAM}$ has been the subject of intense investigation. For the low-spin m^o form, there is indication that at least one axial ligand is cysteinyl sulfur; this evidence is in part from EPR spectra of synthetic low-spin ferric heme-thiol compounds, whose electronic g values simulate closely those of m^o.[7a,8] More recent pulsed EPR measurements[7b] suggest that histidine may be the remaining, second, axial ligand for m^o. Pulsed NMR studies[1] showed marked enhancement of water proton relaxation by m^o, an enhancement most unusual for low-spin ferric heme systems. Interpretation of the proton relaxation data by the Solomon-Bloembergen equations[9] implies the presence of one or more strongly coupled exchangeable protons within 2.6–2.9 Å of the m^o heme iron.[10] This result rules out an axially coordinated histidine as the site of the exchangeable proton(s). The more directly interpretable ENDOR method provides further information about the exchangeable protons. The ligand field in the high-spin component of m^{os}, by all available evidence, retains the axial coordination of cysteinyl sulfur. Studies of a synthetic $Fe^{III}(PPIXDME)(SC_6H_4NO_2)$ complex have strongly supported this assignment.[8] The synthetic complex has a five-coordinate structure with a thiolate sulfur axial ligand and a rhombic EPR g tensor comparable with that of high-spin m^{os}. Determination of coordination and bond distances of high-spin cytochrome P450 by EXAFS (extended X-ray absorption fine structure) has been complicated by the presence of a minority low-spin ferric component.[11] With EPR and ENDOR, however, one can select features specific to high-spin ferric m^{os}, e.g., the g_z = 1.79 extremum which is undisturbed by a low-spin ferric component.

Low-spin m^o has principal g values of g_x = 1.91, g_y = 2.26, g_z = 2.45.[12] The ENDOR signal[13] of m^o [14] in Figure 1 was obtained near the g_z extremum. In protonated medium m^o gave a broad set of ENDOR resonances near 8 and 16 MHz, which were absent in deuterated m^o. (We have noted some splitting of these broad features, particularly near 16 MHz; thus, there could be either two slightly different exchangeable protons on a given m^o molecule or two slightly different binding sites for the same proton.) The coupling to the exchangeable proton(s) is maximal at g_z. Previous ENDOR observations on low-spin ferric heme systems gave heme-nitrogen resonances in the 1–6-MHz region and some weakly coupled protons, but in low-spin systems ENDOR from strongly coupled, exchangeable protons, as in m^o, had never been observed.[15]

To interpret proton ENDOR obtained at g_z, a first-order expression is used:[15c,d] $\nu_{ENDOR} = \nu_{NMR} \pm (1/2)A_{zz}$, where ν_{NMR} is the free proton NMR frequency and A_{zz} is the component of proton hyperfine coupling along the g_z axis. To first order one expects to see pairs of proton ENDOR lines centered at ν_{NMR} and split apart by the magnitude of A_{zz}. For the exchangeable protons of Figure 1, A_{zz} is 8–9 MHz. A_{zz} will have two contributions: i.e., $A_{zz} = A_{iso} + A_{dipole}$, where A_{iso} is the

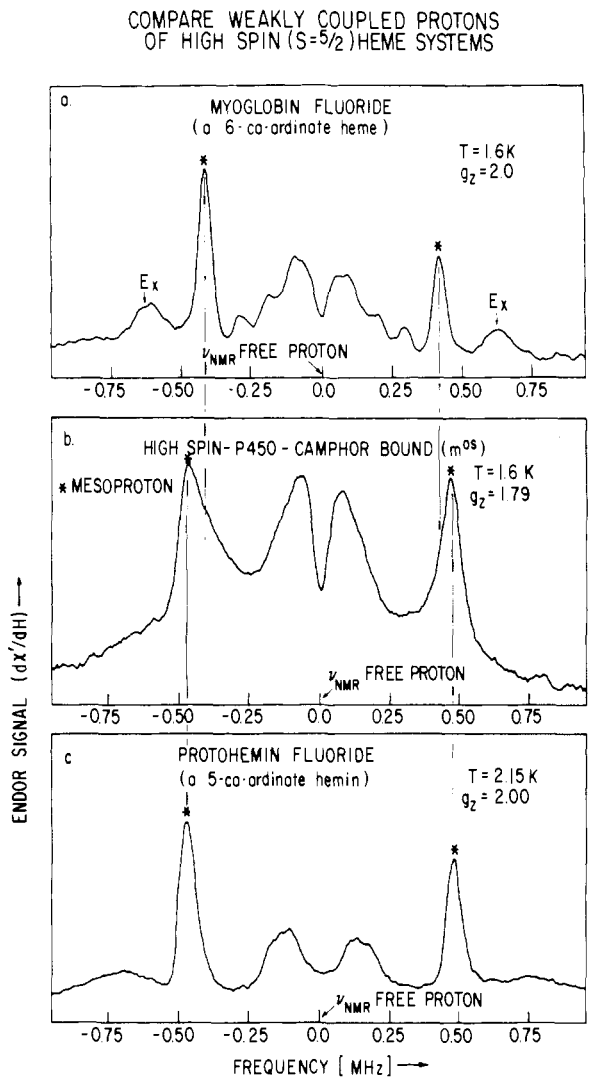

Figure 3. Weakly coupled proton ENDOR spectra of (a) six-coordinate metmyoglobin fluoride, (b) high-spin ferric m^{os}, and (c) five-coordinate hemin fluoride. The starred peaks are assigned to heme meso protons. The spectra of metmyoglobin fluoride and hemin fluoride are essentially identical with those presented elsewhere (Figure 2c[15d] and Figure 4,[15c] respectively). The cytochrome $P450_{CAM}$ sample is identical with that given in Figure 2. These spectra are referred to the respective free proton frequencies: ~14.0 MHz for the fluoride derivatives and 15.5 MHz for the m^{os}. Each spectrum took ~1 h of signal averaging.

Fermi contact term, estimated as 2.2–3.1 MHz from proton relaxation,[1b] and A_{dipole} is the magnetic dipolar contribution, given to first order in eq 2 of ref 15d. In m^{o}, if the maximum g value (g_z) points near the normal to the heme, as previously found for other low-spin ferric heme proteins,[16] one would expect the dipolar interaction for a proton on the axial ligand to be maximal at g_z. The dipolar coupling for a proton 2.6–2.9 Å along the g_z = 2.45 axis is computed to be +7 to +10 MHz. Thus, the sum of dipolar plus contact interaction predicted from proton relaxation work, including a possible ambiguity in sign of the contact interaction, is in agreement with the hyperfine coupling observed by ENDOR for the strongly coupled, exchangeable proton(s). In principle these proton(s) could be from H_2O, from amino acid side chains of the form RNH_2, ROH, or $RCONH_2$, or, conceivably, from an exchangeable proton bound to cysteinyl sulfur. The δ-N proton on histidine is an unlikely candidate for the observed 8–9-MHz splitting; this proton would be ~5 Å from the heme iron and have a dipolar coupling of only ~1.3 MHz.[17]

High-spin m^{os} has principal g values of g_x = 8, g_y = 4, g_z = 1.8.[12] The ENDOR spectrum at the g_z extremum is compared in Figure 2 with that of high-spin aquometmyoglobin. Single-crystal EPR on aquometmyoglobin and fluorometmyoglobin has indicated that the minimum g value, g_z, is perpendicular to the heme plane.[16a,18] Besides the ENDOR from heme nitrogens[15a] and nonexchangeable protons,[15d] the metmyoglobin resonances have been assigned to proximal histidine nitrogen[15a] and to exchangeable water protons of the distal, sixth, ligand.[15d] In high-spin m^{os} no ENDOR resonances attributable to histidine nitrogen or to any exchangeable protons were observed. A new, broad, nonexchangeable proton was seen with hyperfine coupling of ~4 MHz.

We have previously found in high-spin ferric heme systems detailed ENDOR spectra within ±1 MHz of the free proton frequency.[15c,d] In Figure 3 this region of the ENDOR spectrum of m^{os} is compared with the spectra of fluorometmyoglobin and hemin fluoride, typical six- and five-coordinate high-spin ferric heme systems, respectively. By model studies, the sharp, starred features have previously been assigned to heme meso protons.[15c] In the six-coordinate systems, the hyperfine couplings to meso protons were in the 0.79–0.83-MHz range[15c,d,19] and, in the five-coordinate hemins so far studied, the values were greater, i.e., in the 0.95–1.01-MHz range.[15c,20] In m^{os} the coupling to the meso protons is 0.93 ± 0.01 MHz, i.e., close to the coupling in the high-spin ferric five-coordinate systems. Finally we point out that in the fluorometmyoglobin the peaks marked "EX" are due to exchangeable protons assigned to the δ-N proton of the proximal histidine.[15d] No such proton signals are observed in high-spin m^{os}. Thus, the lack of ENDOR from commonly found aquo and histidine ligands and the similarity of the m^{os} meso proton splitting to that seen from five-coordinate hemins point to five coordination of heme iron in m^{os}.

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(20) Proto- and deuterohemin esters were studied[15c] as the five-coordinate, axially liganded derivatives. To prevent aggregation, a solvent mixture containing $CHCl_3$-CH_2Cl_2 plus diamagnetic mesoporphyrin ester was used. With the corresponding ferric derivatives of octaethylporphyrin, $CHCl_3$-CH_2Cl_2 alone will suffice to prevent aggregation, and the meso proton couplings observed are identical to within 0.02 MHz with those from the respective five-coordinate proto- and deuterohemins.

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Applications of Light-Induced Electron-Transfer Reactions: Generation and Reaction of Ag^0 in Solution via Visible Light Photolysis of $Ru(bpy)_3^{2+}$

Sir:

Several investigations have shown that the effective oxidizing and reducing power of excited states of a wide variety of compounds including aromatic hydrocarbons, dyes, and transition-metal complexes is increased upon electronic excitation by an amount effectively equal to the relaxed excited-state energy.[1-5] Thus for excited states of a complex such as the much investigated tris(2,2'-bipyridine)ruthenium(II)$^{2+}$, $Ru(bpy)_3^{2+}$, reduction of substrates having potentials $E_{1/2}[S^{n+/(n-1)+}] \geq -0.81$ V is energetically favorable and generally extremely rapid with typical rates near the diffusion controlled limit.[3] Examination of polarographic data suggests that Ag^+ might be expected to be a good substrate for oxidative quenching of $Ru(bpy)_3^{2+*}$ since its half-wave reduction potential is in the range of +0.4 to +0.8 V[6] where rapid and efficient reduction is expected. However, measured reduction potentials for Ag^+ link the cation and metallic solid; when the reduction is carried out in dilute homogeneous solution, the initial species generated should be atomic silver which is clearly of much higher energy and likely of different reactivity than the metal. In the present paper, we report a study of quenching of $Ru(bpy)_3^{2+*}$ by Ag^+ in acetonitrile and aqueous solution. Our results indicate that effective quenching does occur but with much lower rates than predicted by reduction potentials. The results further indicate that the reduced silver species generated is extremely reactive and suggest that the techniques used can be extended for the generation and study of dispersed reactive atomic species by oxidation or reduction of other soluble ions.

Irradiation of solutions containing $Ru(bpy)_3^{2+}$ and $AgNO_3$, $AgClO_4$, or $Ag(bpy)_2^+$ in acetonitrile or water with visible or near-UV light results in quenching of the strong $Ru(bpy)_3^{2+}$ luminescence but no permanent chemistry.[7,8] For both solvent systems, linear Stern-Volmer plots are obtained with low to moderate concentrations of Ag^+. However, in aqueous solution there is a positive deviation with Ag^+ concentrations >1.5 M which suggests some ground-state complex formation at these levels.[9] Quenching constants obtained are 1.1×10^5 M^{-1} s^{-1} for both $AgNO_3$ and $AgClO_4$ in acetonitrile and 3.5×10^6 M^{-1} s^{-1} for $AgClO_4$ in water. The silver(I) complex, $Ag(bpy)_2^+$, is a somewhat better quencher in acetonitrile giving $k_q = 1.5 \times 10^6$ M^{-1} s^{-1}. Although no permanent products are formed at high Ag^+ concentrations, flash photolysis indicates a transient bleaching of the $Ru(bpy)_3^{2+}$ consistent with that observed in other cases where oxidative quenching occurs;[3,11] the regeneration of the spectrum follows equal concentration second-order kinetics giving $k_r = 5.5 \times 10^9$ and 1.2×10^{10} M^{-1} s^{-1} for $AgNO_3$-acetonitrile and $AgClO_4$-water, respectively. While no permanent products are produced in these cases, addition of low concentrations (1×10^{-2} M) of triethylamine [in the range where quenching of $Ru(bpy)_3^{2+*}$ by triethylamine is negligible][12] to solutions containing $Ru(bpy)_3^{2+}$ and $AgNO_3$ or $AgClO_4$ in acetonitrile results in the formation of colloidal silver or silver mirrors upon irradiation with visible-near-UV light. A study of the irradiation of acetonitrile solutions of $Ru(bpy)_3^{2+}/AgNO_3$ in an ESR cavity at 25 °C led to no detectable signals either in the absence or presence of triethylamine.

The results are most consistent with a transient reduction of Ag^+ ions by the excited complex, $Ru(bpy)_3^{2+*}$, as outlined in eq 1-6. Reaction 2 has been previously studied via pulse radiolysis techniques and found to have a rate constant of $k_2 = 5.9 \times 10^9$ M^{-1} s^{-1};[13] thus, under conditions used in the present study, conversion of Ag^0 to Ag_2^+ should dominate all other reactions and the observed back-reaction most likely is that given by eq 3. Addition of triethylamine has been previously shown to scavenge the oxidized complex, $Ru(bpy)_3^{3+}$, in competition with the normal back-electron transfer (eq 3 and 4);[14] in this case the use of the scavenger permits Ag_2^+ to survive long enough for agglomeration or aging processes leading to metallic silver to occur.

$$Ru(bpy)_3^{2+*} + Ag^+ \rightarrow Ru(bpy)_3^{3+} + Ag^0 \quad (1)$$

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (2)$$

$$Ag_2^+ + Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{2+} + 2Ag^+ \quad (3)$$

$$Ru(bpy)_3^{3+} + Et_3N: \rightarrow Ru(bpy)_3^{2+} + Et_3N^+ \quad (4)$$

$$Et_3N^+ \cdot \rightarrow \text{products} \quad (5)$$

$$Ag_2^+ \rightarrow \rightarrow Ag_{(s)} \quad (6)$$

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