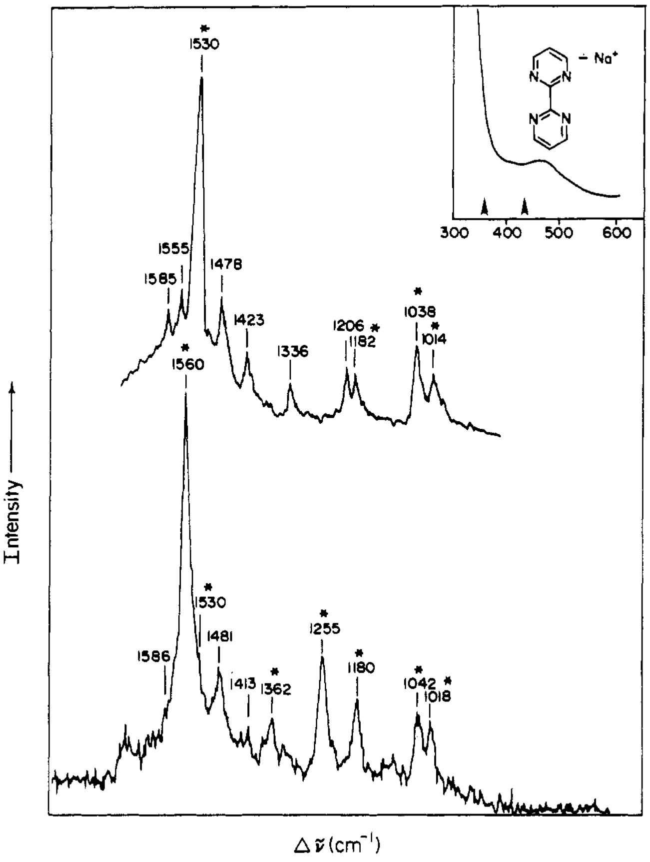

Figure 2. Resonance Raman spectra of deoxygenated 10^{-3} M aqueous solutions of $Ru^{II}(bpym)_3Cl_2$: top frame, under pulsed excitation at 440.0 nm; bottom frame, under pulsed excitation at 354.7 nm. Wavenumber shifts are given above the peaks. Bands attributed to (MLCT) excited-state scattering are marked with asterisks. [Inset: Absorption spectrum (300–600 nm) of Na^+bpym^- in THF, with $Ru(bpym)_3^{2+}$ pulsed excitation wavelengths denoted by arrows.]

under 364-nm CW excitation (Figure 1, bottom frame); however, their relative intensities are markedly different—note the three highest frequency peaks in particular—and two weak new bands are observed, at 1070 and 1120 cm^{-1}. The enhancement pattern has changed, which shows that two (or more) excited states are differently in resonance at the two excitation wavelengths.

Raman spectra of $Ru(bpym)_3^{2+}$ excited by relatively high-power pulses at approximately the same wavelengths as the CW experiments are reproduced in Figure 2. Scattering from an excited electronic state is clearly evident in both cases. Consider first the blue excitation (top frames). Ground-state peaks are still evident in Figure 2 with the same relative intensities shown in Figure 1, but the pulse-excited spectrum is dominated by new peaks at 1014, 1038, 1182, and 1530 cm^{-1}, which are denoted by asterisks in Figure 2. These new bands are also observed under pulsed UV excitation (Figure 2, lower frame). However their relative intensities differ somewhat from those observed under 440-nm irradiation, and there are three new excited-state peaks, at 1255, 1362, and 1560 cm^{-1}. (Some ground-state scattering also contributes to the peak at 1560 cm^{-1}; see relative intensities in bottom frame of Figure 1.) We attribute the excited-state scattering to complexes having one of the bidentate ligands in the MLCT state: $Ru^{III}(bpym)_2(bpym^{-}\cdot)^{2+}$. This model, in which on the vibrational time scale the excitation is localized on one of the ligands, is well established for 2,2′-bipyridine (bpy) complexes of Ru and Os.[6] Our Raman data indicate that different upper electronic states are in resonance with the MLCT-excited tris(bipyrimidine)ruthenium complex at the two excitation wavelengths employed. This is consistent with the electronic absorption spectrum of Na^+bpym^- in THF (Figure 2, inset), which shows two well-separated transitions.

A complete excitation profile of the $Ru(bpym)_3^{2+}$ ground state and additional resonance Raman spectra of the MLCT-excited state, as well as resonance Raman spectra of the mixed-ligand complex $Ru(bpym)_2(bpy)^{2+}$, will be given in a subsequent publication. The photophysical and photochemical properties of such d^6-transition-metal polypyridine complexes are of great interest because of their potential photosensitization applicability;[7] we have demonstrated here that resonance Raman spectroscopy provides a powerful probe of the relevant excited states.

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Registry No. $Ru(bpym)_3^{2+}$, 80263-32-7.

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Energy-Transfer Quenching of Excited States of Polypyridine Complexes of Ruthenium(II) by Hexaamminecobalt(III) or Tris(ethylenediamine)cobalt(III)

Sir:

Electron transfer and energy transfer are established pathways for the deactivation of luminescent states of (polypyridine)ruthenium(II) complexes.[1] For cobalt(III) complexes both mechanisms were postulated,[2,3] but following Navon and Sutin's demonstration[4] of electron-transfer quenching for pentaamminecobalt(III) complexes, this mechanism was tacitly assumed to be operative for all cobalt(III) complexes.[1,5] However, each system must be investigated in detail in order to reach a sound mechanistic assignment. As an illustration, we cite the identification of both energy- and electron-transfer pathways from quenching and quantum yield studies with cobalt(III) cage complexes.[6,7]

Recently,[8] the quenching of the luminescence of ruthenium and osmium polypyridine complexes by several cobalt(III) complexes was reported and interpreted as electron transfer. We have carried out similar studies with three of the complexes studied[8] ($Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(en)_3^{3+}$), but we have also measured quantum yields for Co(II) production. Our results

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Table I. Rate Constants and Quantum Yields of Co(II) for the Quenching of $^*Ru(bpy)_3^{2+}$ by Co(III) Complexes[a]

quencher	$10^7 k_q$, $M^{-1}\,s^{-1}$ [b]	ϕ [c]	N_{Co} [d]
$Co(en)_3^{3+}$	3.4 ± 0.3[e,f]	(2.1–2.4) × 10^{-3}	0.11 ± 0.02[g,h]
$Co(NH_3)_6^{3+}$	1.5 ± 0.2[i,j]	(4.5–4.6) × 10^{-3}	0.45 ± 0.03[k,l]
$Co(NH_3)_5Cl^{2+}$	38 ± 2[k]	(0.18–0.19)	1.05 ± 0.06[k,m]

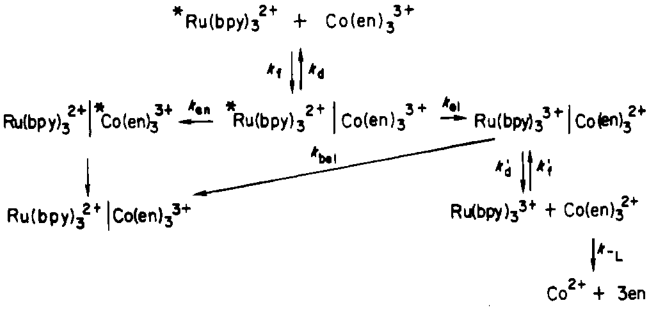
[a] At 25 °C, pH 4.7 (acetate), and ionic strength 0.01 M (NaCl); deaerated solutions. [b] From emission intensities measured in a Perkin-Elmer MPF 44 spectrofluorometer and corrected for absorption according to the equation given by: Leopold, K.; Haim, A. *Inorg. Chem.* **1978**, *17*, 1753. Excitation at 400–450 nm; emission at 610 nm; $[Ru(bpy)_3^{2+}]$ = (2.9–5.2) × 10^{-6} M; [Co(III)] = (3.0–90) × 10^{-4} M. [c] Quantum yield of Co^{2+}. Irradiation at 450 nm; $[Ru(bpy)_3^{2+}]$ = 5.1 × 10^{-5} M; [Co(III)] = (1.0–1.1) × 10^{-3} M. [d] Quantum yield of Co^{2+} corrected for unquenched $^*Ru(bpy)_3^{2+}$. [e] Average of eight sets of independent measurements. [f] One set of measurements in 0.10 M H_2SO_4 yielded 4.9 × 10^7 $M^{-1}\,s^{-1}$ (450-nm excitation), 5.0 × 10^7 $M^{-1}\,s^{-1}$ (400-nm excitation), and 5.4 × 10^7 $M^{-1}\,s^{-1}$ (400-nm excitation, saturated air), in poor agreement with the value 2.0 × 10^7 $M^{-1}\,s^{-1}$ reported in ref 8. [g] Average of three measurements. [h] One measurement in 0.010 M HCl gave N_{Co} = 0.11. Two measurements in the presence of 5.0 × 10^{-5} M ascorbic acid gave N_{Co} = 0.11 and 0.14. [i] Average of six sets of independent measurements. [j] One set of measurements in 0.10 M H_2SO_4 yielded 3.2 × 10^7 $M^{-1}\,s^{-1}$ (450-nm excitation), 3.1 × 10^7 $M^{-1}\,s^{-1}$ (400-nm excitation), and 3.2 × 10^7 $M^{-1}\,s^{-1}$ (400-nm excitation, saturated air), in reasonable agreement with the value 4.0 × 10^7 $M^{-1}\,s^{-1}$ reported in ref 8. [k] Average of two measurements. [l] One measurement in the presence of 5.0 × 10^{-5} M ascorbic acid gave N_{Co} = 0.43. [m] Our value is in agreement with the value 0.86 ± 0.15 reported in ref 4 but not with the value 0.52 ± 0.21 reported by: Finkenberg, E.; Fisher, P.; Huang, S.-M. Y.; Gafney, H. D. *J. Phys. Chem.* **1978**, *82*, 526.

Table II. Rate Constants for Reductions of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ [a]

reductant	$k_{Co(NH_3)_6^{3+}}$, $M^{-1}\,s^{-1}$	$k_{Co(en)_3^{3+}}$, $M^{-1}\,s^{-1}$ [b]	ratio	ref
Cr^{2+}	1.0 × 10^{-3}	3.4 × 10^{-4}	2.9	*c*
V^{2+}	1.0 × 10^{-2}	7.2 × 10^{-4} (4.0 × 10^{-3})	14	*c*
Eu^{2+}	2.6 × 10^{-3}	4.0 × 10^{-4}	6.5	*d*
Yb^{2+}	2.2 × 10^{3}	4.5 × 10^{2}	4.9	*e*
U^{3+}	1.32	0.133	9.9	*f*
$Cr(bpy)_3^{2+}$	2.5 × 10^{2}	63 (3.8 × 10^{2})	4.0	*g*
$Ru(NH_3)_6^{2+}$	2.3 × 10^{-2}	4.8 × 10^{-3} (4.2 × 10^{-3})	4.8	*d*, *h*
$Ru(en)_3^{2+}$	4.4 × 10^{-4}	2.0 × 10^{-6} (4.3 × 10^{-4})	220	*d*
$Co(sep)^{2+}$	0.9	4.7 × 10^{-2} (0.22)	19	*c*
$Co(sar)^{2+}$	2.3	1.1 (1.5)	2.1	*i*
MV^+	1.2 × 10^{6}	2.3 × 10^{5}	5.2	*j*
$^*Ru(bpy)_3^{2+}$	1.5 × 10^{7}	3.4 × 10^{7} (1.3 × 10^{7})	0.44	*k*
$^*Ru(5\text{-}Clphen)_3^{2+}$	3.2 × 10^{7}	4.8 × 10^{7}	0.67	*k*
$^*Ru(phen)_3^{2+}$	4.6 × 10^{7}	6.5 × 10^{7}	0.71	*k*
$^*Ru(5,6\text{-}dimephen)_3^{2+}$	5.3 × 10^{7}	9.1 × 10^{7}	0.55	*k*
$^*Ru(4,7\text{-}dimephen)_3^{2+}$	7.7 × 10^{7}	1.1 × 10^{8}	0.70	*k*

[a] At 25 °C and variable acidity and ionic strength; rate constants for a given reductant at same ionic strength. [b] Value in parentheses calculated from Marcus' cross-relationship when exchange parameters are available. [c] Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545. [d] Reference 15. [e] Christenson, J. H.; Espenson, J. H.; Butcher, A. B. *Inorg. Chem.* **1973**, *12*, 564. [f] Wang, R. T.; Espenson, J. H. *J. Am. Chem. Soc.* **1971**, *93*, 380. [g] Zwickel, A. M.; Taube, H. *Discuss. Faraday Soc.* **1960**, *29*, 42. [h] Hammershoi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979. [i] Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022. [j] MV^+ = methylviologen radical. Measured in the present work by a flash photolytic technique: Böttcher, W.; Haim, A. *Inorg. Chem.* **1982**, *21*, 531. [k] Present work. The values of *k* represent quenching constants.

Scheme I



demonstrate that the dominant quenching mechanism for $Co(en)_3^{3+}$ is energy transfer, that comparable contributions of electron and energy transfer obtain in $Co(NH_3)_6^{3+}$, and that, in agreement with Navon and Sutin,[4] the sole detectable pathway for $Co(NH_3)_5Cl^{2+}$ is electron transfer. Since our interpretation for the hexaamine complexes differs from that published,[8] we report herein the results of our work.

Intensity quenching measurements yielded linear Stern–Volmer plots, and the derived values of k_q are listed in column 2 of Table I. Quantum yields for Co(II) production, measured by steady-state photolysis,[9] are listed in column 3 of Table I. Correction of the quantum yields for the fraction of unquenched $^*Ru(bpy)_3^{2+}$ gives N_{Co} (column 4, Table I), the number of Co^{2+} ions produced per quenching event.

To account for $N_{Co} < 1$, various plausible mechanisms are embodied in Scheme I. (1) Quenching of $^*Ru(bpy)_3^{2+}$ by $Co(en)_3^{3+}$ (or $Co(NH_3)_6^{3+}$) proceeds via parallel energy- (k_{en}) and electron- (k_{el}) transfer pathways. With $k_d' >> k_{bel}$, N_{Co} equals $k_{el}/(k_{el} + k_{en})$. (2) Only electron-transfer quenching obtains, but back-electron-transfer (k_{bel}) in the solvent cage competes favorably with cage separation (k_d').[10] With $k_{-L} >> k_f'$, N_{Co} equals $k_d'/(k_d' + k_{bel})$. (3) Only electron-transfer quenching obtains and is followed by cage separation, but back-reaction between the free $Co(en)_3^{2+}$ and $Ru(bpy)_3^{3+}$ competes successfully with ligand loss (k_{-L}) from $Co(en)_3^{2+}$. With $k_d' >> k_{bel}$, $N_{Co} = k_{-L}/(k_{-L} + (k_f'/k_d')k_{bel}[Ru(bpy)_3^{3+}])$.

Mechanism 3 is ruled out by comparing the rate constants for ligand detachment from $Co(en)_3^{2+}$ ($k_{-L} \sim 7 \times 10^2\ s^{-1}$)[11] and for the $Co(en)_3^{2+}$–$Ru(bpy)_3^{3+}$ reaction ($k_f'k_{bel}/k_d' \sim 5 \times 10^6\ M^{-1}\,s^{-1}$).[12] Since $Ru(bpy)_3^{3+}$ undergoes rapid spontaneous reduction under the conditions utilized for the quantum yield measurements, its maximum concentration is estimated at ~10^{-6} M.[13] Therefore, the rate of the $Co(en)_3^{2+}$–$Ru(bpy)_3^{3+}$ reaction (~$5[Co(en)_3^{2+}]$) is smaller than that for ligand loss from $Co(en)_3^{2+}$ (~$7 \times 10^2[Co(en)_3^{2+}]$). Evidently, back-electron-transfer between free $Co(en)_3^{2+}$ and $Ru(bpy)_3^{3+}$ cannot compete with ligand detachment, and therefore mechanism 3 cannot provide an explanation for the low yield of Co(II). An additional argument against mechanism 3 comes from the observation (cf. Table I, footnote

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(9) At the end of the desired irradiation time, an aliquot of the photolyzed solution was diluted 5-fold and then added to a column of Dowex 50-X8 (100–200 mesh, Na^+ form). The Co(II) absorbed on the column was eluted with 5 × 10^{-4} M Na_2EDTA in 0.02 M, pH 5 acetate buffer. The Co(II) in the eluant was analyzed spectrophotometrically with Nitroso R salt.

(10) A variation of this mechanism involves production of an unstable low-spin CoA_6^{2+}, and the competition is between back-electron-transfer and cage separation and/or spin deactivation. However, this mechanism can be ruled out on energetic grounds. The couple CoA_6^{3+}/low-spin CoA_6^{2+} is, after correcting to the zero–zero difference, about 0.8 V more negative than the couple CoA_6^{3+}/high-spin CoA_6^{2+}: Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304. Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014. Therefore, the $^*Ru(bpy)_3^{2+}$–$Co(NH_3)_6^{3+}$ and $^*Ru(bpy)_3^{2+}$–$Co(en)_3^{3+}$ reactions, which yield the low-spin cobalt(II) complexes, have $\Delta E°$ values of ~0.1 and ~−0.1 V, respectively, and it is highly unlikely that such nearly ergoneutral reactions could proceed with rate constants near $10^8\ M^{-1}\,s^{-1}$.

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(13) Note that steady-state irradiations are carried out for 12–14 h. The steady-state concentration of $Ru(bpy)_3^{3+}$ was computed from the light intensity (~3 × 10^{-9} einstein/s) absorbed by a 31-mL solution in a 10-cm cell and the known[14] rate of reaction of $Ru(bpy)_3^{3+}$ with water.

h) that the quantum yield of Co^{2+} is unaffected by the addition of ascorbic acid. Since the $Ru(bpy)_3^{3+}$–ascorbic acid reaction is almost diffusion controlled and the concentration of ascorbic acid is much higher than that of $Co(en)_3^{2+}$, the $Co(en)_3^{2+}$–$Ru(bpy)_3^{3+}$ reaction could not compete with the ascorbic acid–$Ru(bpy)_3^{3+}$ reaction. We could not measure the rate of the $Co(NH_3)_6^{2+}$–$Ru(bpy)_3^{3+}$ reaction.[14] However, although the rate for oxidation of $Co(NH_3)_6^{2+}$ by $Ru(bpy)_3^{3+}$ is probably[15] ~10 times faster than for oxidation of $Co(en)_3^{2+}$, the rate of ligand detachment for $Co(NH_3)_6^{2+}$ is also considerably faster ($k_{-L} > 7 \times 10^5$ s^{-1}). Undoubtedly, ligand loss from $Co(NH_3)_6^{2+}$ is considerably faster than oxidation by $Ru(bpy)_3^{3+}$, and mechanism 3 is also ruled out for $Co(NH_3)_6^{3+}$.

Mechanism 2 is ruled out by comparing the rate constants for cage separation ($k_d' \sim 1 \times 10^{10}$ s^{-1}, estimated from theoretical equations[16]) and for cage recombination ($k_{bel} \sim 1 \times 10^7$ s^{-1} estimated from the measured value $k_f'k_{bel}/k_d' = 5 \times 10^6$ M^{-1} s^{-1} and the calculated[16] value $k_f'/k_d' \sim 0.5$ M^{-1}). Evidently, cage recombination is much slower than cage separation and cannot account for the low yield of Co(II) for $Co(en)_3^{2+}$. Similarly, assuming that the rate of oxidation of $Co(NH_3)_6^{2+}$ is ~10 times faster than for $Co(en)_3^{2+}$,[15] cage recombination is too slow to compete with cage separation and mechanism 2 is ruled out for $Co(NH_3)_6^{3+}$ as well.

Our conclusion that mechanism 1, parallel energy- and electron-transfer pathways, is operative for quenching of $^*Ru(bpy)_3^{2+}$ by $Co(en)_3^{3+}$ or $Co(NH_3)_6^{3+}$ receives additional support by recognizing that reactions of $Co(NH_3)_6^{3+}$, which proceed by electron transfer, are *invariably* faster than those of $Co(en)_3^{3+}$ (Table II).[15] The *observed* rate constants for quenching of $^*Ru(bpy)_3^{2+}$ (and other (polypyridine)ruthenium(II) complexes) exhibit the opposite order, but when corrected for the energy-transfer contribution, the resulting *electron-transfer* quenching constants, 3.7×10^6 and 6.8×10^6 M^{-1} s^{-1} for $Co(en)_3^{3+}$ and $Co(NH_3)_6^{3+}$, respectively, conform to the normal reactivity pattern. The energy-transfer pathway demonstrated for $Co(en)_3^{3+}$ and $Co(NH_3)_6^{3+}$ quenching of $^*Ru(bpy)_3^{2+}$ does not imply that the other Co(III) complexes studied by Sandrini et al.[8] also react by energy transfer. In fact, for $Co(NH_3)_5Cl^{2+}$ (with $N_{Co} = 1.05 \pm 0.06$, Table I) and in general for the more reactive complexes,[7] the predominant, if not exclusive, pathway for deactivation of $^*Ru(bpy)_3^{2+}$ may well be electron transfer.

Finally we comment on the reported nonadiabatic factors of 0.1, 1×10^{-3}, and 1×10^{-5} for a variety of redox and quenching reactions of $Co(NH_3)_6^{3+}$ (and $Co(NH_3)_5OH_2^{3+}$), $Co(en)_3^{3+}$, and $Co(phen)_3^{3+}$ (and $Co(bpy)_3^{3+}$). Although the fits of the homogenized[17] rate constants to an empirical[18] dependence of $\Delta G^*(0)$ upon $\Delta G°$ are acceptable, we question the reliability of the derived values of κ and ΔG^* in the equation[17] $k = (k_d/k_{-d})(kT/h)\kappa\cdot\exp(-\Delta G^*/RT)$. First, combination of the fitted values[8] of κ and ΔG^* and the estimated[8] values of k_d and k_{-d} yields second-order rate constants of self-exchange for $Co(NH_3)_6^{3+/2+}$ (and $Co(NH_3)_5OH_2^{3+/2+}$), $Co(en)_3^{3+/2+}$, and $Co(phen)_3^{3+/2+}$ (and $Co(bpy)^{3+/2+}$) of 3.2×10^{-6}, 4.4×10^{-3}, and 3.8×10^{-2} M^{-1} s^{-1}, compared with experimental values of $\sim 1 \times 10^{-6}$, 7.7×10^{-5}, and 4.2×10 M^{-1} s^{-1}. We regard any treatment of cross-reactions that is incompatible with the experimentally measured self-exchange rate constants and does not explain the discrepancy as suspect.[19] Second, the rate constants for quenching of $^*Ru(bpy)_3^{2+}$ by $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Co(phen)_3^{3+}$ [20] include contributions of energy transfer and, unless these contributions are subtracted, any treatment of the quenching constants as electron-transfer rate constants is flawed. Third, we note that the average ratio of $k_{Co(NH_3)_6^{3+}}/k_{Co(en)_3^{3+}}$ for the *redox* reactions listed in Table II (excluding[15] $Ru(en)_3^{2+}$) is 7 ± 5, in excellent agreement with the value of ~10 estimated from the adiabatic equation[21] $k_{12}/k_{13} = [k_{22}(\Delta E_{23}°)/k_{33}]^{1/2}$. Moreover, the values of $k_{Co(en)_3^{3+}}$ agree within a factor of less than 6 (excluding[15] $Ru(en)_3^{2+}$) with the calculated values utilizing Marcus' cross-reaction (ion-pair model), allowing for little nonadiabaticity in the reactions listed. In contrast, the reactions of the Co(II) complexes with $Ru(bpy)_3^{3+}$ appear to be nonadiabatic, as previously noted[7] for the corresponding reactions of Co(II) cage complexes.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(NH_3)_5Cl^{2+}$, 14970-14-0.

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Organosilicates as Silica Surface Models: The Molybdenum Trioxide Complexes $R_3SiOMoO_3^-$, Where R = Phenyl and *tert*-Butyl

Sir:

Molybdenum trioxide supported on silica can serve as a catalyst or a catalyst precursor for a variety of reactions,[1] including the partial oxidation of alkanes,[2,3] alkenes,[4] and alcohols;[5] olefin metathesis;[6] and thiophene hydrodesulfurization.[7] Despite numerous attempts to characterize MoO_3/SiO_2,[8] the active chemical species remain obscure due to the insoluble and amorphous nature of the material and the absence of well-characterized compounds that model its spectroscopic and chemical properties. As part of a more general program concerned with modeling oxide surface hydroxyl groups, we have begun to investigate the synthesis, characterization, and reactivity of organosilicate–molybdate complexes. The simplest conceivable complexes of this type, $R_3SiOMoO_3^-$ ($R = C_6H_5$, t-C_4H_9), are reported here as crystalline $(n\text{-}C_4H_9)_4N^+$ salts that are soluble and indefinitely stable in aprotic media.

Following the classical method of preparing MoO_3/SiO_2 from SiO_2 and aqueous $(Mo_7O_{24})(NH_4)_6$,[9] we have treated 0.05 M

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