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Luminescence and Intramolecular Energy-Transfer Processes in Isomeric Cyano-Bridged Rhenium(I)–Rhenium(I) and Rhenium(I)–Ruthenium(II)–Rhenium(I) Polypyridyl Complexes

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Mixed-metal and homometal cyano-bridged polypyridyl complexes of Re(I) and Ru(II) such as $[(CO)_3(bpy)Re-CN-Re(bpy)(CO)_3]^+$, $[(CO)_3(bpy)Re-NC-Ru(bpy)_2-CN-Re(bpy)(CO)_3]^{2+}$, and $[(CO)_3(bpy)Re-CN-Ru(dcbpy)_2-NC-Re(bpy)(CO)_3]^{2+}$ (bpy = 2,2′-bipyridine and dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) have been synthesized. Their spectroscopic, redox, and photophysical properties are reported. The lowest energy CT excited state in these complexes (Re–bpy or Ru–bpy CT) is emissive in fluid solutions. In the trinuclear complexes, intense absorption in the infrared region corresponding to intervalence (IT) transitions are reported in the CT excited state and partially oxidized species. Luminescence and redox properties have been used to assess intramolecular energy/electron-transfer processes between the terminal Re(I)–polypyridyl and central Ru(II)–polypyridyl units. The intervalence transitions and the excitation spectra for the Ru-based emission suggest efficient occurrence of energy transfer from the CT excited state of the Re-based chromophore to the Ru-based unit in both complexes $[(CO)_3(bpy)Re-NC-Ru(bpy)_2-CN-Re(bpy)(CO)_3]^{2+}$ and $[(CO)_3(bpy)Re-CN-Ru(dcbpy)_2-NC-Re(bpy)(CO)_3]^{2+}$. A comparison is made between the N- and C-bonded isomers and also between Re–Ru–Re– and Ru–Ru–Ru–polypyridyl trinuclear complexes.

Introduction

Studies on polynuclear ("supramolecular") complexes comprise an area of growing research interest in several laboratories.[1] A long-term goal of these studies is construction of "light harvesting units" capable of absorbing the entire visible light of the solar spectrum and processing the light energy into useful chemical energy. The efficiency of light harvesting depends on unidirectional flow of incident light energy. The nature of the bridge and the mode of linkage in these complexes influence strongly the communication ("electronic coupling") between the constituent units. In the case of weak interactions, the properties of the "supramolecule" are simply the sum of their constituent units (*localized description*). In the limit of strong interactions, the complexes must be regarded as *delocalized* electronic species with properties quite different from those of their monomeric analogs. Photophysical studies on model compounds can provide important information on intramolecular electron- and energy-transfer processes and clues for an intelligent design of the "antenna" supramolecule. In this work, we focus attention on the possible excited-state interactions (intramolecular energy transfer?) in polynuclear complexes containing Re(I)–carbonyl–polypyridyl and Ru(II)–polypyridyl units. The lowest excited states of these chromophoric units are known to be CT in character and emissive in fluid solutions, and their photophysics is fairly well characterized.

In one major approach modeled on the work of Taube et al.,[2] polyaza aromatics such as pyrazine (pz), bipyrimidine (bpym), dpp,[3] etc. are used as bridges to link different chromophoric or donor–acceptor units. Photophysical data are available on a number of dpp, bpym, or related ligand-bridged polynuclear polypyridyl complexes of Ru(II), Os(II), Re(I), and Cr(III). The literature in this area is extensive,[1] and for some examples of recent studies see refs 4–10. Pertinent to the present work are the reports[5c,6d,10] on the properties of homonuclear complexes of Re(I), $[(LL)(CO)_3Re-BL-Re(LL)(CO)_3]^{2+}$, and mixed-metal complexes containing Re(I) and Ru(II) centers, $[(LL)(CO)_3Re-BL-Ru(LL)_2]^{3+}$ (BL = dpp, bpym, $Me_2bpy-(CH_2)_n-Me_2bpy$;

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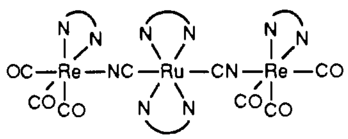
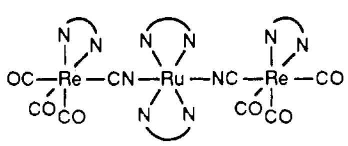
LL = bpy, etc.). In binuclear complexes with bridging ligands such as dpp[5c,10c,10f] or bpym,[6d,10a,10f] the emission of the lowest CT excited state occurs in a region which renders the assignment of the emission difficult. In the case of BL = dpp,[5c] the emitting state has been assigned to a Ru–BL CT transition. Recently, intramolecular energy transfer between the CT excited states of Re(I)–carbonyl–polypyridine and Ru(II)–polypyridyl units has been reported[10b,h] in the complex $[(py)(CO)_3Re(bpyen)Ru(bpy)_2]^{3+}$, bpyen = 1,2-bis(4′-methyl-2,2′-bipyrid-4-yl)ethane.

In an alternate approach, the ability of cyano ligand to act as a bridging ligand has been utilized to construct polynuclear complexes of the type, $-NC-M_1-CN-M_2-NC-$.[11,12] In addition to the basic information that these complexes provide in areas such as mixed-valence species and long-range electron- and energy-transfer processes, they have potential applications to serve as visible light harvesting "antenna units" in sensitization processes. In fact, interest in our laboratories comes from this latter area. Cyano-bridged complexes of the type $[NC-(bpy)_2Ru-CN-Ru(dcbpy)_2-NC-Ru(bpy)_2-CN]^{2+}$ have been found to be excellent photosensitizers in TiO_2-based photoelectrochemical cells.[12e,13]

In the first instance, different metal centers (or chromophoric units) attached to two sides of a C≡N ligand are expected to be strongly coupled. But a number of studies have shown that the two chromophores do behave as distinct entities with characteristic photophysical and redox properties. Studies of complexes containing Ru(II)–CN–Rh(III) and Ru(II)–CN–Cr(III) units recently have shown[14] that "these complexes span a wide range of donor–acceptor couplings". In homobinuclear and -trinuclear complexes containing $Ru(bpy)_2$ units[12] the properties of the Ru(II)–polypyridyl units depend strongly on the mode of coordination of the bridging cyanide ligands. For example, in $[NC-Ru(bpy)_2-CN-Ru(bpy)_2-NC-Ru(bpy)_2-CN]^{2+}$ the energy of the CT excited state associated with the central N-bonded Ru(II) is lower than that of the terminal C-bonded Ru(II) units. In this work, we examine this latter point in detail, using a cyano-bridged binuclear Re(I)–CN–Re(I) complex and isomeric trinuclear complexes of Ru(II) and Re(I) of the following type:





In mixed-metal complexes of Ru(II)- and Re(I)–polypyridyl units, there are independent MLCT transitions associated with each chromophoric unit. The absorptions associated with the Ru(II) centers are dominant (intense by a factor of 2–3), and this tends to mask the Re–bpy CT transitions. However, one can have an estimate using mononuclear and homobinuclear complexes containing these metal centers as model compounds. In polypyridyl complexes containing CN ligands, the excited-state-derived Re–bpy CT is much higher in energy than that of Ru–bpy. Thus, the ambiguous situation observed with polyimine-bridged systems is avoided.

All the cyano-bridged Re–Re and Re–Ru–Re complexes examined in this work are highly emissive. Steady-state luminescence and time-resolved transient absorption techniques have been used to determine the photophysical properties. The absorption spectra of the CT excited state and partially oxidized species have been found to have strong absorptions in the infrared region. These absorptions corresponding to intervalence transitions (IT) indicate very efficient electronic coupling of the chromophoric units through the cyanide bridge. These along with electrochemical data are used to assess the importance of intramolecular energy- and electron-transfer processes in these complexes. With excited states that are M → L charge transfer in character, optical excitation in the CT band creates a hole in the corresponding metal center. Like the chemically oxidized metal center, this transient hole in turn can give rise to intervalence transitions with the adjacent nonoxidized metal centers. Detection of such intervalence transition bands in the excited-state absorption spectra of polynuclear complexes containing MLCT excited states is of much mechanistic interest. Herein we present the absorption spectra of IT in the excited state, and a comparison is made with those observed with chemically generated mixed-valence compounds.

Experimental Section

Synthesis of the Complexes. Commercial $Ru(bpy)_2Cl_2$ and $Re(CO)_5Cl$ were obtained from Strem and Pierce Chemicals, respectively. The precursor complexes such as $Ru(bpy)_2(CN)_2$, $[Re(CO)_3(bpy)(Cl)]$, and $[Re(CO)_3(bpy)(CF_3SO_3)]$ were synthesized by using literature procedures.[13a,15]

Cyanotricarbonyl(2,2′-bipyridine)rhenium(I), $Re(CO)_3(bpy)(CN)$. A 462-mg amount (0.001 mol) of $Re(CO)_3(bpy)(Cl)$ was dissolved in 50 mL of acetone under Ar in the dark. To this solution was added 260 mg (0.001 mol) of $AgCF_3SO_3$ and the reaction mixture allowed to reflux for 1 h. During this period, a white precipitate of AgCl formed. The reflux was then stopped, the solution allowed to cool, and the AgCl precipitate filtered out. The filtrate containing $[Re(CO)_3(bpy)(CF_3SO_3)]$ was carefully transferred to a three-necked flask, and to the solution was added 5-fold excess of KCN (325 mg, 0.005 mol) dissolved in 2 mL of water. Refluxing was carried out for 3 h, after which the solvent was removed under reduced pressure. The resulting solid product was collected on a sintered glass crucible and washed copiously with water, water–acetone (10:1), and ether. The yield of the desired product was 340 mg (75%). Anal. Calcd for $[Re(CO)_3(bpy)(CN)]\cdot 2.5H_2O$: C, 33.80; H, 2.63; N, 8.44. Found: C, 33.67; H, 2.54; N, 8.01.

(μ-Cyano)bis{tricarbonyl(2,2′-bipyridine)rhenium(I)} Trifluoromethanesulfonate, $[(CO)_3(bpy)Re-CN-Re(bpy)(CO)_3]$(triflate). This complex was prepared by refluxing together $[Re(CO)_3(bpy)(CN)]$ (0.452 g) and $[Re(CO)_3(bpy)(CF_3SO_3)]$ (0.575 g) in acetone for 3 h. The desired complex was precipitated by adding diethyl ether. The crude product was recrystallized from acetone/ether. Yield: 700 mg (69%). Anal. Calcd for $[(CO)_3(bpy)Re-CN-Re(bpy)(CO)_3](CF_3SO_3)\cdot 2H_2O$: C, 31.60; H, 1.88; N, 6.58. Found: C, 31.72; H, 1.89; N, 5.91.

Tetrakis(2,2′-bipyridine)-1κ^2N,N';2κ^2N,N';3κ^2N,N',3κ^2N,N'-hexacarbonyl-1κ^3C,2κ^3C-bis(μ-cyano)-1:3$\kappa^2N:C$;2:3$\kappa^2N:C$-1,2-rhenium(I)-3-ruthenium(II) Trifluoromethanesulfonate, $[(CO)_3(bpy)Re-NC-Ru(bpy)_2-CN-Re(bpy)(CO)_3](triflate)_2$. A 46-mg amount (0.001 mol) of $Ru(bpy)_2(CN)_2$ was dissolved in acetone under an Ar atmosphere. To this solution, 287 mg of $Re(CO)_3(bpy)(CF_3SO_3)$ was added and the mixture refluxes for 4 h. The reaction mixture was then allowed to cool to room temperature and filtered through a fine-porosity glass crucible. The filtrate was evaporated under reduced pressure, and the resulting solid was collected on a sintered glass crucible and washed successively with diethyl ether and water in order to remove the excess of $Re(CO)_3(bpy)(CF_3SO_3)$ and $Ru(bpy)_2(CN)_2$ left over. Yield: 113 mg. This crude complex was purified on a neutral alumina column using acetonitrile as the eluant. Anal. Calcd for $[(CO)_3(bpy)Re-NC-Ru(bpy)_2-CN-$

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Re(bpy)(CO)$_3$](CF$_3$SO$_3$)$_2$·3H$_2$O: C, 35.92; H, 2.29; N, 8.39. Found: C, 35.55; H, 2.33; N, 8.13.

Bis(2,2′-bipyridine)-1κ^2*N,N′*;2κ^2*N,N′*-hexacarbonyl-1κ^3*C*,2κ^3*C*-bis(μ-cyano)-1:3κ^2*C*:*N*;2:3κ^2*C*:*N*-bis(4,4′-dicarboxy-2,2′-bipyridine)-3κ^2*N,N′*;3κ^2*N,N′*-1,2-rhenium(I)-3-ruthenium(II) Trifluoromethanesulfonate, [(CO)$_3$(bpy)Re–CN–Ru(dcbpy)$_2$–NC–Re(bpy)(CO)$_3$](triflate)$_2$. A 71-mg amount of Ru(dcby)$_2$Cl$_2$, dcbpy = 4,4′-dicarboxy-2,2-bipyridine, was dissolved in 50 mL of acetone and 5 mL of 0.1 M NaOH in the dark. To this purple solution was added an acetone solution of 113 mg of Re(CO)$_3$(bpy)(CN). The reaction mixture was allowed to reflux for 3 h (though there were no spectral changes after 30 min of refluxing). After this period, the solvent was removed under reduced pressure on a rotary evaporator. The resulting solid product was dissolved in water, and the mixture was filtered in order to remove any insoluble Re(CO)$_3$(bpy)(CN) reactant. The desired trinuclear complex was precipitated from the filtrate as a neutral salt (at pH 2.5–3.5) by adding dilute perchloric or trifluoromethanesulfonic acid. The flask was left in a refrigerator for 12 h. The solid product was filtered through a fine-porosity sintered glass crucible, and after being washed with cold water and acetone, recovered and air-dried. The yield was 60%. Anal. Calcd for [(CO)$_3$(bpy)Re–CN–Ru(dcbpy)(dcbpyH$_2$)–NC–Re(bpy) (CO)$_3$]·10H$_2$O: C, 37.20; H, 3.34, N, 8.36. Found: C, 35.82; H, 3.22, N, 8.02. Along with the complex containing the simple bpy ligand, this dcbpy derivative is referred to as being dicationic. This is true only in acidic solutions (pH ≤ 2). In neutral or alkaline solutions (pH > 4), the carboxyl groups are deprotonated and the complex is dianionic.

Apparatus and Methods. UV–visible absorption spectra were recorded either on a Cary 5 or HP 8450 diode-array spectrophotometer. Infrared spectra were recorded in KBr pellets and as solutions in methylene chloride with a Perkin-Elmer IR instrument. Emission spectra were recorded with a Spex Fluorolog spectrofluorometer equipped with a R2658 Hamamatsu photomultiplier tube and photon counting detection. Significant response of this PM tube in the red near-IR region allows acquisition of corrected emission spectra up to 1000 nm on a routine basis. All the emission spectra were corrected by calibrating the instrumental response with respect to a NBS standard quartz tungsten-halogen lamp.

The emission lifetimes were measured with a J&K system 2000 laser flash photolysis system (frequency-doubled Nd laser, 530 nm, pulse width of 15 ns). The detection unit consists of a Hamamatsu R928 PM (or SHS-100 Si-based photodiode of EG&G) interfaced to a Tektronix 7612 transient digitizer and HP 300 series computer. Low-temperature emission spectra were measured using Oxford Instruments cryostatic equipment with quartz windows and 1-cm cuvettes. A few lifetime measurements were also made using a Photochemical Research Associates nanosecond fluorescence lifetime measurement unit based on single photon counting techniques. Estimated accuracies in the reported absorption and emission maxima are ±3 nm, lifetimes ±10%, and quantum yields ±20%.

Cyclic voltammograms of DMF solutions containing about 10^{-3} M of the complex and 0.1 M TBAP were run on a PAR 362 potentiostat using a conventional three-electrode assembly: a saturated calomel electrode (SCE) (separated from the test solution by a frit) served as the reference electrode, a Pt wire served as the counter electrode, and a Pt wire or glassy carbon served as the working electrode. Square wave voltammetric studies were made on a BAS100 electrochemical analyzer (Bioanalytical Systems). Solutions were deaerated with ultrapure nitrogen for at least 10 min prior to measurements. Reported redox potentials are vs SCE, and the estimated accuracies in these are ±20 mV.

Results and Discussion

I. Synthesis and Characterization of the Complexes. Two types of polynuclear complexes involving cyanide as the bridging ligand have been studied in this work: Carbonyl bipyridine complexes of Re(I), [(CO)$_3$(bpy)Re]$_n$(CN) (n = 1, 2), and heterotrinuclear complexes involving Ru(II) and Re(I), [(CO)$_3$(bpy)Re–NC–Ru(bpy)$_2$–CN–Re(CO)$_3$(bpy)]$^{2+}$ and [(CO)$_3$(bpy)Re–CN–Ru(dcbpy)$_2$–NC–Re(CO)$_3$(bpy)]$^{2+}$. Procedures employed in the synthesis of various Re, Re–Re, and Re–Ru–Re compounds are standard coupling schemes, largely inspired from the work of Meyer et al.[10d,g,15b] These are outlined in reactions 1–6. Replacement of the chloride in [Re(CO)$_3$(bpy)(Cl)] (**1**) using silver triflate leads to formation of the crucial compound, the triflate complex of Re, [Re(CO)$_3$(bpy)(trif)] (**2**):

$$\mathrm{Re(CO)_5Cl + bpy \xrightarrow{\Delta/\text{toluene}} Re(CO)_3(bpy)Cl + 2CO} \tag{1}$$

$$\mathrm{Re(CO)_3(bpy)Cl + Ag(trif) \xrightarrow{\text{acetone}} Re(CO)_3(bpy)(trif) + AgCl} \tag{2}$$

Replacement of the facile leaving triflate ligand by cyanide ligand leads to formation of [Re(CO)$_3$(bpy)(CN)] (**3**)

$$\mathrm{Re(CO)_3(bpy)(trif) + KCN \xrightarrow[\text{water}]{\text{acetone/}} Re(CO)_3(bpy)(CN) + K(trif)} \tag{3}$$

Instead of KCN, metal complexes containing cyanide ligand such as [Re(CO)$_3$(bpy)(CN)] or [Ru(bpy)$_2$(CN)$_2$] can also be used to obtain the complexes [Re$^{\mathrm{I}}$-CN-Re$^{\mathrm{I}}$] (**4**) and [Re$^{\mathrm{I}}$-NC-Ru$^{\mathrm{II}}$-CN-Re$^{\mathrm{I}}$] (**5**), respectively:

$$\mathrm{Re(CO)_3(bpy)(trif) + Re(CO)_3(bpy)(CN) \xrightarrow{\text{acetone}} [(CO)_3(bpy)Re{-}CN{-}Re(CO)_3(bpy)](trif)} \tag{4}$$

$$\mathrm{2Re(CO)_3(bpy)(trif) + Ru(bpy)_2(CN)_2 \xrightarrow{\text{acetone/water}} [(CO)_3(bpy)Re{-}NC{-}Ru(bpy)_2{-}CN{-}Re(CO)_3(bpy)](trif)_2} \tag{5}$$

The cyano complex of Re, **3**, can also be reacted with Ru(LL)$_2$Cl$_2$ to obtain the isomeric trinuclear complexes [Re$^{\mathrm{I}}$–CN–Ru$^{\mathrm{II}}$–NC–Re$^{\mathrm{I}}$] (**6**, **7**):

$$\mathrm{[Ru(LL)_2Cl_2] + 2Re(CO)_3(bpy)(CN) \xrightarrow{\text{alkaline acetone}} [(CO)_3(bpy)Re{-}CN{-}Ru(LL)_2{-}NC{-}Re(CO)_3(bpy)]Cl_2} \\ \mathrm{LL = dcbpy\ (\mathbf{6}),\ bpy\ (\mathbf{7})} \tag{6}$$

To our knowledge, complexes **3**–**6** are new, and they are characterized by a number of physical methods (e.g., elemental analysis, IR spectra, and comparison of absorption and emission properties with those of the starting materials). [During the course of the preparation of this manuscript, Leasure et al.[16] have reported on the excited-state acid–base chemistry of the complexes Re(CO)$_3$(LL)(CN) with LL = bpy, phen, etc. For the bpy complex, our photophysical data are in excellent agreement.]

Mono- and binuclear tricarbonyl–polypyridyl–Re(I) complexes examined in this work are pale yellow in color. Except for **6** (see discussion below), all other complexes are stable as solids and in solutions at room temperature (protected from ambient light). Table I presents a summary of the absorption maxima and molar extinction coefficients in fluid solutions for various Re complexes examined in this work. In a localized-valence description, various Re and Re/Ru complexes examined herein will have the ruthenium atoms of the bis(bipyridine) unit in the +2 state and the rhenium in the tricarbonyl bipyridine unit in the +1 state.

For complexes containing carbonyl and/or cyano ligands, IR spectra are highly informative of the structure.[10,12,14] Table II contains a collection of the relevant IR frequencies in the carbonyl and cyanide stretching region for various complexes measured in this work. In addition to these listed ones, all complexes show typical IR bands for the presence of bpy: ≈1602 cm^{-1} (δ_{ring}); ≈1467, ≈1477, and ≈1421 cm^{-1} ($\nu_{\mathrm{C=C}}$, $\nu_{\mathrm{C=N}}$). The tricarbonyl chloro complexes, Re(CO)$_3$(LL)Cl, have three bands at ca. 2015, 1920, and 1890 cm^{-1}, assigned to the facial arrangement of the carbonyl groups. This feature is reproduced in all the cyano-substituted complexes **3**–**6**: [(CO)$_3$(LL)Re]$_n$(CN), n = 1, 2; [Re$^{\mathrm{I}}$–NC–Ru$^{\mathrm{II}}$–CN–Re$^{\mathrm{I}}$]; [Re$^{\mathrm{I}}$–CN–Ru$^{\mathrm{II}}$–NC–Re$^{\mathrm{I}}$].

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(16) Leasure, R. M.; Sacksteder, L.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722.

Table I. Absorption Spectral Properties of Re Complexes (Triflate Salts) in Methylene Chloride Solutions (Except As Noted) at Room Temperature

	maxima (nm) (ϵ (M^{-1} cm^{-1}))				
complex	Ru–LL CT	Re–LL CT	π–π^*	π–π^*	π–π^*
$Re(CO)_3(bpy)(Cl)$ (**1**)		386 (3540)	320 sh	294 (18 100)	256, 242
$Re(CO)_3(bpy)(CN)$ (**3**)		380 (3450)	319 sh	294 (14 500)	244
$[(bpy)Re–CN–Re(bpy)]^+$ (**4**)		370 (6610)	319 sh	292 (31 200)	242
$[Re–NC–Ru–CN–Re]^{2+}$ (**5**)	442 (8060)	337 sh (12 300)	318 sh	292 (58 800)	244
$[Re–CN–RuNC–Re]^{2+}$ (**6**)[a]	500 (12 600)	366 (16 900)	308 (60 100)	302 sh	243

[a] Neutral complex dissolved in alkaline ethanol.

Table II. IR Stretching Frequencies for the Carbonyl and Cyanide Groups in Re(I) Complexes

	frequency (cm^{-1})			
complex	CN(terminal)	CN(bridged)	CO	ref[a]
	Mononuclear Complexes			
$Re(CO)_3(bpy)(Cl)$ (**1**)			2020, 1917, 1898	10
$Re(CO)_3(bpy)(trif)$ (**2**)			2040/2025, 1935/1920, 1900	tw
$Re(CO)_3(bpy)(CN)$ (**3**)	2120 w		2025/2010, 1915, 1895	tw
$Ru(bpy)_2(CN)_2$	2053, 2067			12
	2060, 2072			14
	2060, 2070			tw
	Binuclear Complexes			
$[Re–CN–Re]^+$ (**4**)		2150	2025, 1920, 1890	tw
(NC)Ru–CN–Ru(CN)	2069	2098		12b
(NC)Ru–CN–Pt	2058	2108		11c
(NC)Ru–CN–Rh	2067	2108		14
Ru–NC–Cr(CN)	2050	2132		14
	Trinuclear Complexes			
$[Re–NC–Ru–CN–Re]^{2+}$ (**5**)		2120/2100	2025, 1915, 1890	tw
$[Re–CN–Ru–NC–Re]^{2+}$ (**6**)[b]			2030, 1920, 1890	tw
$[Re–CN–Ru–NC–Re]^{2+}$ (**7**)			2030, 1925, 1890	tw
Pt–NC–Ru–CN–Pt		2129/2108		11c
Rh–NC–Ru–CN–Rh		2124/2105		14
(NC)Ru–CN–Ru–NC–Ru(CN)	2073	2099		12b
	2065	2100		tw

[a] tw = this work. [b] Bis-4,4′-dcbpy ligands on Ru.

In cyano-bridged complexes, the IR bands for the CN stretch allow differentiation of the terminal cyanide groups from those that are bridging. $Ru(bpy)_2(CN)_2$ has two IR bands at 2053 and 2067 cm^{-1}, characteristic of two monodentate cyanide groups, in a cis configuration. Coordinating the cyanide with another metallo fragment leads to shifting of these stretching frequencies to higher energies. $[(bpy)_2(NC)Ru–CN–Ru(CN)(bpy)_2]$, for example, shows two well-separated bands, one corresponding to monodentate cyanide (at 2058 cm^{-1}) and the other at 2108 cm^{-1} for the bridging cyanide. Trinuclear complexes with two cyanide bridges such as M–NC–Ru–CN–M (M = Rh, Pt) have been reported to show two bands (at 2108 and 2129 cm^{-1}) corresponding to two bridging cyanide groups in a cis configuration. The trinuclear complex with two bridging cyanides, $[Re^I–NC–Ru^{II}–CN–Re^I]$, shows two bands at 2125 and 2100 cm^{-1}, in good agreement with earlier literature reports.

The cyanide ligand attached to the Re(I) center in $Re(CO)_3(bpy)(CN)$ has its C–N stretch located at 2120 cm^{-1}. The bridging cyanide in the binuclear complex Re–CN–Re has its IR stretch at 2150 cm^{-1}. The 30-cm^{-1} difference between the terminal and bridging cyanide observed in Re complexes compares well with similar magnitude shifts observed in cyano-bridged complexes of Ru, Rh, Pt, and Cr.

II. Isomerization and Stability of Cyano-Bridged Complexes. On the trinuclear complexes with N-bonded Ru(II) centers, discussions will refer mostly to **6**. Repeated attempts to prepare authentic sampls of the analogous complex **7** with bpy ligands attached to Ru were unsuccessful. Refluxing of $Re(CO)_3(bpy)(CN)$ with $[Ru(bpy)_2(H_2O)]^{2+}$ gives rise to distinct color changes. Reaction mixtures were examined using luminescence as a guide. Formation of highly luminescent $Ru(bpy)_2(CN)_2$ can be observed after a short-time reflux. The latter is formed presumably by dissociation of CN^- ligands from the Re complex and subsequent attachment to Ru(II) centers. Extensive reflux (several hours) of such solutions leads to formation of the other isomer, viz. complex **5**.

$$2Re(CO)_3(bpy)(CN) + [Ru(bpy)_2(H_2O)_2]^{2+} \rightarrow 2[Re(bpy)(CO)_3(H_2O)]^+ + [Ru(bpy)_2(CN)_2] \quad (7)$$

Stirring of the two reactants ($Re(CO)_3(bpy)(CN)$ with $[Ru(bpy)_2(H_2O)]^{2+}$) in the dark at ambient temperature (over 24 h) also gives rise to the formation of detectable amounts of $Ru(bpy)_2(CN)_2$. Thus, it appears that ligand isomerization is thermally assisted. The higher stability of the Ru–CN bond with respect to the Re–CN bond is in agreement with the observed IR frequencies. Crude samples of **7** gave absorption and emission spectral data qualitatively similar to that of complex **6**. Due to the problems of stability and emission from impurities, we have not included any discussion on complex **7**.

Surprisingly, thermal cleavage and related isomerization however have not been observed during the synthesis of the analogous dcbpy complex **6** and the C-bonded complex **5**. Solutions of **5** and **6** in water and various organic solvents are quite stable in the dark at least for 24 h. Solutions of **6** in organic solvents (such as acetonitrile or methylene chloride) however undergo photoinduced isomerization. Significant photolysis was observed even under ambient light. These solutions need to be protected from light, and measurements are made preferably with freshly prepared solutions. Detailed studies of quantum yields and the mechanism of the photoinduced cleavage and isomerization are currently in progress and results will be reported on a later date.

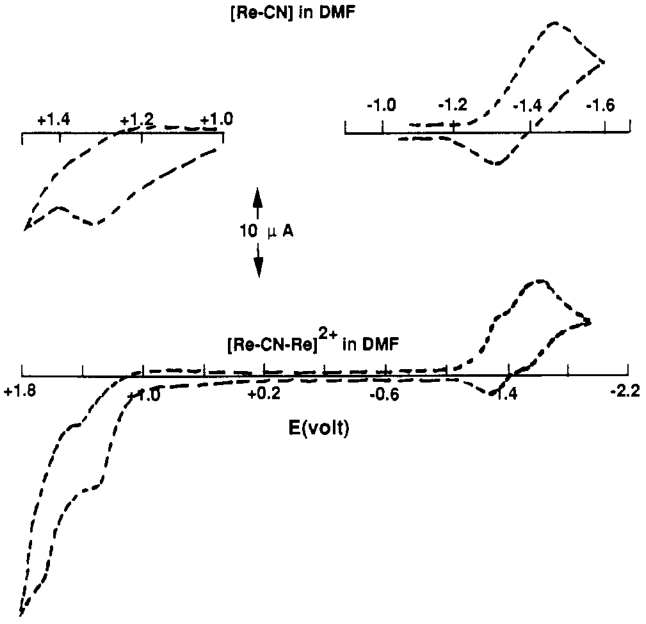

Figure 1. Cyclic voltammograms for $Re(CO)_3(bpy)(CN)$ (top) and $[(bpy)(CO)_3Re{-}CN{-}Re(CO)_3(bpy)]^+$ (bottom) in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) (scan rate = 50 mV/s). Potentials indicated are vs SCE.

There have been a number of reports in the 1960s[17] on the thermal linkage isomerization of cyano-complexes involving 3d metals. The isomerization in all cases starts with the cleavage of an M–CN bond. As far as cyano-bridged Ru complexes are concerned, in a footnote,[12] Scandola and co-workers have noted the occurrence of thermal isomerization in $[\mathrm{Cr^{III}{-}CN{-}Ru^{II}{-}NC{-}Cr^{III}}]$ complexes. The sustained observation of emission from $Ru(bpy)_2(CN)_2$ after repeated attempts of purification has also been noted in a related, recent study[14] on $[\mathrm{Rh^{III}{-}NC{-}Ru^{II}{-}CN{-}Rh^{III}}]$ complexes. Unfortunately thermal and photoassisted isomerization and cleavage of the type noted above are serious problems that limit the utility of complexes of this type.

III. Electrochemical Studies of Cyano-Bridged Complexes. Electrochemical studies of the mononuclear and binuclear complexes allowed identification of one or more oxidation and reduction waves. Figure 1 shows the cyclic voltammograms for the mono- and binuclear Re(I) complexes in CH_3CN. Data are summarized in Table III. The first oxidation and reduction of mononuclear complexes $Re(CO)_3(bpy)(Cl)$ and $Re(CO)_3(bpy)(CN)$ occur at nearly identical potentials. The reversible one-electron reduction of the mononuclear complex has an anodic–cathodic peak separation of 70 mV. In the binuclear complex, two reduction waves with midpoint potentials of −1.29 and −1.41 V can be observed. (Actually the reduction waves overlap but square wave voltammetry has resolved these two overlapping waves into two separate peaks of equal intensity.) These are tentatively assigned to the reduction of bpy ligands attached to Re(I) centers that are C- and N-bonded, respectively.[18] The first oxidation at a potential of +1.35 V is tentatively assigned to the Re center that is N-bonded. The second oxidation at +1.60 V is assigned to Re(I) that carries the C-bonded cyanide (eq 8). The successive oxidations of the two Re centers are irreversible, as evident from the absence of cathodic part of these waves during slow/moderate scans (up to 100 mV/s).

$$[\mathrm{Re^{I}{-}NC{-}Re^{I}}] \xrightarrow{1.35\ \mathrm{V}} [\mathrm{Re^{II}{-}NC{-}Re^{I}}] \xrightarrow{1.60\ \mathrm{V}} [\mathrm{Re^{II}{-}NC{-}Re^{II}}] \qquad (8)$$

The 250-mV peak separation between the N- and C-bonded Re units can arise from a combination of two factors: (i) The N-end of the cyanide, as an amine type ligand, acts as a strong σ-donor. Coordination through this nitrogen may create higher electron density around the Re center, causing easier oxidation when compared to its C-bonded analog. (ii) Mere electrostatic effects comprise the second factor; i.e., first oxidation in the binuclear complex leads to increase of overall charge from +2 to 3, while second oxidation would cause further increase of charge to +4. Similar results have been obtained earlier for Ru–CN–Ru complexes.[12]

Cyclic voltammetric studies of complex **5** showed several reduction waves. Figure 2 shows square wave voltammetric curves measured in DMF. The first one, a 2-electron wave at −1.23 V, is assigned to reduction of the bpy ligand of the two terminal Re(I) chromophores. This is followed by successive reduction of bpy ligands of the central Ru chromophore at −1.57 and −1.84 V, respectively. By analogy to the cyano-bridged Re/Re and Ru/Ru complexes, the first oxidation at ≈1.0 V is assigned to the central Ru(II) followed by oxidation of the peripheral Re(I) centers (eq 9).

$$[\mathrm{Re^{I}{-}NC{-}Ru^{II}{-}CN{-}Re^{I}}] \xrightarrow{1.00\ \mathrm{V}} [\mathrm{Re^{I}{-}NC{-}Ru^{III}{-}CN{-}Re^{I}}] \qquad (9a)$$

$$[\mathrm{Re^{I}{-}NC{-}Ru^{III}{-}CN{-}Re^{I}}] \xrightarrow{1.40\ \mathrm{V}} [\mathrm{Re^{II}{-}NC{-}Ru^{III}{-}CN{-}Re^{I}}] \qquad (9b)$$

Electrochemical measurements on the complex **6** in DMF showed several reduction waves. The first reduction occurs at −1.30 V. From symmetry considerations of the complex it is attributed to reduction of bpy ligand(s) attached to terminal Re(I) centers. The second reduction wave, observed at −1.70 V (a one-electron wave), is assigned to reduction of bpy attached to central Ru(II). The first oxidation occurs with a midpoint potential of +0.75 V and is assigned to oxidation of the central Ru(II) carrying two N-bonded cyanide ligands (eq 10).

$$[\mathrm{Re^{I}{-}CN{-}Ru^{II}{-}NC{-}Re^{I}}] \xrightarrow{0.75\ \mathrm{V}} [\mathrm{Re^{I}{-}CN{-}Ru^{III}{-}NC{-}Re^{I}}] \qquad (10a)$$

$$[\mathrm{Re^{I}{-}CN{-}Ru^{III}{-}NC{-}Re^{I}}] \xrightarrow{1.40\ \mathrm{V}} [\mathrm{Re^{II}{-}CN{-}Ru^{III}{-}NC{-}Re^{I}}] \qquad (10b)$$

The oxidation of the central N-bonded Ru(II) in the trinuclear complex $[\mathrm{Ru^{II}{-}CN{-}Ru^{II}{-}NC{-}Ru^{II}}]^{2+}$ has been reported[12] to occur at similar potentials (+0.74 V). A summary of the measured redox potentials along with their assignments is included in Table III.

IV. Photophysics of mononuclear and Homobinuclear Complexes of Re(I). Figure 3 presents the absorption and emission spectra of mono- and binuclear Re complexes $[(CO)_3(bpy)Re]_n(CN)$ (n = 1, 2) in methylene chloride in ambient temperature. The spectral features are similar to those reported earlier for complexes of this kind.[15] The prominent absorption bands are Re–bpy CT in the 360-nm region and intraligand (π–π^*) transitions at ca. 319, 292, and 244 nm. The CT absorption band blue shifts upon replacement of the Cl^- ligand by CN^- (386 to 380 nm) and upon formation of the binuclear complex (380 to 370 nm). The 370-nm CT band in the binuclear complex is considerably broad (with molar absorbances nearly twice), as compared to the parent mononuclear complex. Emission lifetimes and relative quantum yields have been measured in various solvents both at ambient temperature and in low-temperature glasses (77 K, ethanol–methanol, 4:1 v/v). These data are summarized in

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[17] (a) Brown, D. B.; Shriver, D. F.; Schwartz, L. H. *Inorg. Chem.* **1968**, *7*, 77. (b) House, J. E.; Bailer, J. C.; *Inorg. Chem.* **1969**, *8*, 672. (c) Birk, J. P.; Espenson, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 1153.

[18] Kitamura, N.; Sato, M.; Kim. H.-B.; Obata, R.; Tazuke, S. *Inorg. Chem.* **1988**, *27*, 651 and references cited therein.

Table III. Redox Potentials along with Their Assignments for Various Mono, Bi-, and Trinuclear Complexes of Re[a]

complex	$E^{ox}(1)^b$	$E^{ox}(2)$	$E_{1/2}^{red}(1)$	$E_{1/2}^{red}(2)$
$Re(CO)_3(bpy)Cl)$ (**1**)	+1.33		−1.34 (LL)	
$Re(CO)_3(bpy)(CN)$ (**3**)	+1.32 (Re_{CN})		−1.36 (LL)	
$[(bpy)Re–CN–Re(bpy)]^+$ (**4**)	+1.35 (Re_{NC})	+1.60 (Re_{CN})	−1.29 ($LL_{Re–C}$)	−1.41 ($LL_{Re–N}$)
$[Re–NC–Ru–CN–Re]^{2+}$ (**5**)[c]	≈1.0 (Ru_{CN})	≥1.4 (Re_{NC})	−1.23[d] (LL_{Re})	−1.57 (LL_{Ru})
$[Re–CN–RuNC–Re]^{2+}$ (**6**)[c]	+0.75 (Ru_{NC})	≥1.4 (Re_{CN})	−1.30[d] (LL_{Re})	−1.70 (NN_{Ru})

[a] All potentials are vs SCE measured in CH_3CN containing 0.1 M TBA(ClO_4) using a glassy-carbon electrode (LL = bpy, NN = dcbpy). [b] Oxidations involving Re centers are irreversible (cf. Figure 1), and shown are the anodic peak potentials. [c] Measured in DMF. [d] 2-electron reduction.

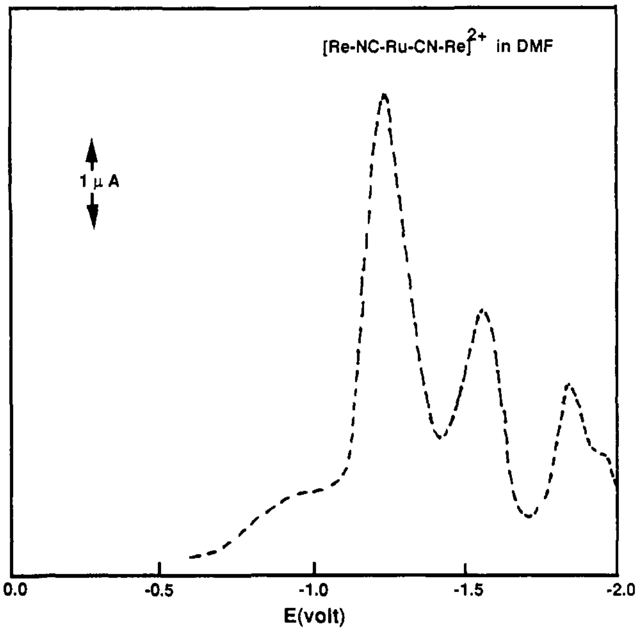

Figure 2. Square wave voltammetric waves for the reduction of $[(bpy)(CO)_3Re–NC–Ru(bpy)_2–CN–Re(CO)_3(bpy)]^{2+}$ in DMF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAP). Potentials shown are vs SCE.

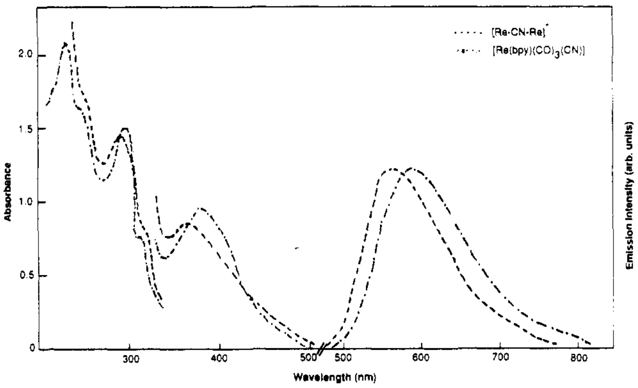

Figure 3. Absorption and emission spectra of $Re(CO)_3(bpy)(CN)$ (2.7×10^{-4} M) and $[(CO)_3(bpy)Re–CN–Re(CO)_3(bpy)]^+$ (1.3×10^{-4} M) in methylene chloride solutions at ambient temperature (293 K).

Table IV. Emission Properties of Re Complexes

		em (room temp)		em (Et–Me, 77 K)	
complex	solvent	max (nm)	τ (ns)	max (nm)	τ (μs)
$Re(CO)_3(bpy)(Cl)$ (**1**)	CH_2Cl_2	622	50	550	2.78
$Re(CO)_3(bpy)(CN)$ (**3**)	CH_2Cl_2	591	160	523	3.33
	CH_3OH	587	140		
	CH_3CN	595	125		
	CH_3COCH_3	599	100		
$[Re–CN–Re]^+$ (**4**)	CH_2Cl_2	571	395	530	3.92
	CH_3OH	581	190		
	EtOH	580			
	CH_3CN	580	245		
$[Re–NC–Ru–CN–Re]^{2+}$ (**5**)	CH_2Cl_2	643	465	592, 602	4.09
	CH_3OH	639	310		
	CH_3CN	645	330		
$[Re–CN–Ru–NC–Re]^{2+}$ (**6**)	EtOH	661	<40		
	H_2O	707		655, 695	
	DMF	670			
$Ru(bpy)_2(CN)_2$	EtOH	659	375	588	4.0
	CH_2Cl_2	678	450		
	CH_3CN	699	275		

Table IV. The observed emission lifetime (160 ns) and quantum yield (≈0.05) for $Re(CO)_3(bpy)(CN)$ in methylene chloride gives a radiative lifetime ($\tau_{rad} = \tau_{obs}/\phi$) of 3.2 μs, in good agreement with earlier estimates.[15b,16] A similar estimate of τ_{rad} = 2.95 μs is obtained for the binuclear complex.

As expected for charge-transfer transitions, the absorption and emission spectra are solvent dependent. For example, the CT band maximum of $Re(CO)_3(bpy)(CN)$ shifts from 359 to 380 nm upon going from acetonitrile (polar) to methylene chloride. The solvent sensitivity is considerably reduced in the binuclear complex (absorption maxima shifts from 360 to 370 nm only). The solvent dependence of the M–bpy CT band in mixed-ligand complexes such as $Ru(bpy)_2(CN)_2$[18] comes largely from H-bonding interactions of the terminal CN ligands. Hence, in the binuclear complex with the bridging cyanide, the solvent sensitivity is much less pronounced.

The absorption and emission bands corresponding to the Re–bpy CT transition blue shift (≈750 cm^{-1}) upon formation of the binuclear complex. If the energies of the Re–bpy CT excited state in the N- and C-bonded Re units were quite different, one would expect two resolved bands in the lowest energy absorption. The 20-nm blue shift in the emission maximum suggests that the energies of these two states differ hardly by 0.1 eV. In a given solvent, the CT excited state of the binuclear complex is much longer-lived as compared to the mononuclear complex. The longer lifetime observed for the higher energy emission is consistent with the expectations of the "energy gap law".[15b]

In both the mono- and binuclear complexes, over the entire emission band, the luminescence decay is exponential (>98%). Thus, in the binuclear complex, there are no indications for discrete emission from the right- and left-side chromophores:

$$[(bpy)Re^I–CN–Re^I(bpy)]^+ \xrightarrow{h\nu} [(bpy)Re^I–CN–Re^{II}(bpy^{\bullet-})]^{+*} \quad (11)$$

$$[(bpy)Re^I–CN–Re^I(bpy)]^+ \xrightarrow{h\nu} [(bpy^{\bullet-})Re^{II}–CN–Re^I(bpy)]^{+*} \quad (12)$$

The emission presumably occurs from two closely-lying levels, equilibrated so as to exhibit a single exponential decay. The observed emission maximum could be an average of emission maxima from the two levels or the relatively weaker, red-shifted emission from the lower-energy CT transition is buried under the more intense emission. The absorption spectra of the two possible chromopores strongly overlap not allowing selective excitation of one.

It is interesting to compare the behavior of these Re complexes with analogous cyano-bridged complexes with Ru(II) polypyridyl units.[12] In the latter case, the absorption maximum of the lowest CT band also blue shifts upon formation of the similar bi- or

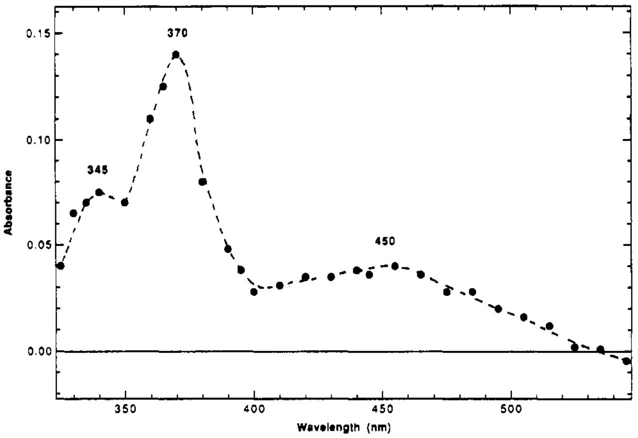

Figure 4. Transient absorption (difference) spectrum corresponding to the Re–bpy CT excited state, recorded during 353-nm laser flash photolysis of $[\mathrm{Re(bpy)(CO)_3]_2(CN)}$ in methylene chloride at 293 K. The spectrum was recorded at 50 ns after laser pulse excitation.

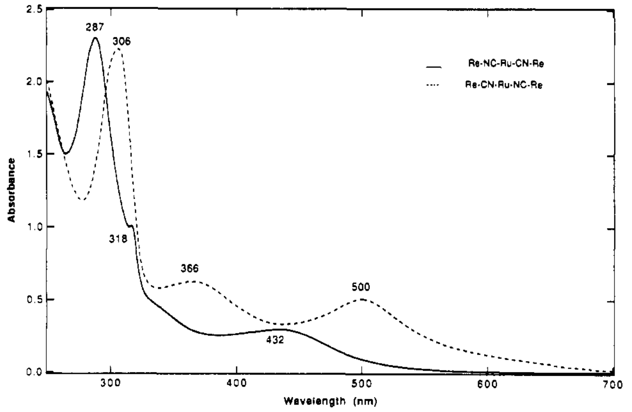

Figure 5. Absorption spectra of the trinuclear complex $[\mathrm{(bpy)(CO)_3Re{-}NC{-}Ru(bpy)_2{-}CN{-}Re(CO)_3(bpy)}]^{2+}$ (**5**) in acetonitrile and $[\mathrm{(bpy)(CO)_3{-}Re{-}CN{-}Ru(dcbpy)_2{-}NC{-}Re(CO)_3(bpy)}]^{2+}$ (**6**) in alkaline water (pH 10) at room temperature (293 K).

trinuclear complexes. But the emission maximum gradually red-shifts (with decreasing lifetimes). The observed emission is assigned in all cases to CT transitions involving N-bonded Ru(II) units. In the present case, the observed emission (though occurring at higher energies) is tentatively assigned to CT transition involving bpy and the N-bonded Re metal center.

Figure 4 presents the transient difference absorption spectrum corresponding to formation of the MLCT excited state in the binuclear complex in methylene chloride solution at room temperature (293 K). The absorption spectrum recorded at 50 ns after 353-nm laser pulse excitation is characterized by maxima at 345, 370, and 450 nm. The spectrum is typical of carbonyl polypyridine complexes of Re(I), $\mathrm{Re(CO)_3(LL)(X)}$.[10d,15] The assignment of the transient absorption as due to the MLCT excited state is based on the matching decay of the transient absorption with the luminescence. In the wavelength range of 320–370 and 420–500 nm, a very small amount of the transient ($\leq 10\%$ of the initial transient absorbance) decays much slowly (decay over ≈ 2 μs). This could possibly be due to some photodecomposition products. The photophysical properties of the binuclear Re–CN–Re complex will be used as a model (reference) to interpret the properties of the Re-based unit in cyano-bridged trinuclear complexes involving Re(I)– and Ru(II)-polypyridyl units.

V. Photophysics of the Complex 5, $[\mathrm{Re^I{-}NC{-}Ru^{II}{-}CN{-}Re^I}]^{2+}$. Figure 5 presents the absorption spectra of the trinuclear complexes **5** in $\mathrm{CH_3CN}$ and **6** in aqueous alkaline ethanol. The complex **5**, $[\mathrm{Re^I{-}NC{-}Ru^{II}{-}CN{-}Re^I}]^{2+}$, has its longest wavelength maximum at 432 nm. Measured absorption maxima and molar extinction coefficients are listed in Table I. On the basis of its intensity and expected energy, the lowest energy absorption band in both complexes is attributed to Ru–LL CT. As noted in the introductory paragraphs, Ru–bpy CT transitions are considerably more intense than those of Re–bpy CT. The absorption band corresponding to Re–bpy CT can be barely detected as a shoulder at ≈ 350 nm in complex **5**. In addition to the CT bands, both the trinuclear complexes have their (π–π^*) bands of bpy/dcbpy at $\approx 287/306$ and 244 nm. In both complexes (**5** and **6**), 530-nm excitation leads to selective population of the Ru-based CT excited state:

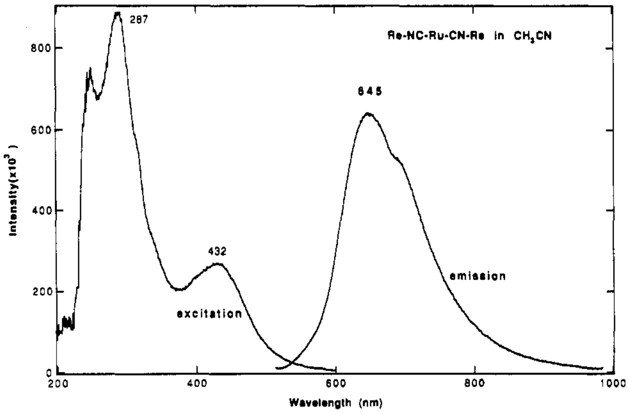

Figure 6. Emission spectrum of the trinuclear complex **5**, $[\mathrm{(bpy)(CO)_3Re{-}NC{-}Ru(bpy)_2{-}CN{-}Re(CO)_3(bpy)}]^{2+}$, in acetonitrile solutions at 293 K ($\lambda_{\mathrm{excit}} = 470$ nm) and excitation spectrum for $\lambda_{\mathrm{em}} = 650$ nm.

$$[\mathrm{Re^I{-}NC{-}Ru^{II}{-}CN{-}Re^I}] \xrightarrow{h\nu} [\mathrm{Re^I}{-}NC{-}Ru^{II}{*}{-}CN{-}\mathrm{Re^I}] \tag{13}$$

For excitation at $\lambda \leq 400$ nm, there will be simultaneous formation of Re(I)- and Ru(II)-based CT excited states:

$$[\mathrm{Re^I{-}NC{-}Ru^{II}{-}CN{-}Re^I}] \xrightarrow{h\nu} [Re^{I}{*}{-}NC{-}\mathrm{Ru^{II}{-}CN{-}Re^I}] \tag{14}$$

This could be followed by intramolecular energy/electron-transfer processes of the type shown in eqs 15 and 16 (en tr = energy transfer; e$^-$ tr = electron transfer).

$$[Re^{I}{*}{-}NC{-}\mathrm{Ru^{II}{-}CN{-}Re^I}] \xrightarrow{\text{en tr}} [\mathrm{Re^I}{-}NC{-}Ru^{II}{*}{-}CN{-}\mathrm{Re^I}] \tag{15}$$

$$[Re^{I}{*}{-}NC{-}\mathrm{Ru^{II}{-}CN{-}Re^I}] \xrightarrow{e^-\ \text{tr}} [\mathrm{Re^0{-}NC{-}Ru^{III}{-}CN{-}Re}] \tag{16}$$

Figure 6 shows the emission spectrum of the complex **5** (the trinuclear complex with Ru(II) centers C-bonded) in acetonitrile solutions at 293 K. Excitation at $\lambda \geq 420$ nm leads to an emission with a maximum at ≈ 645 nm and a quantum yield of ≈ 0.01. Excitation at $\lambda \leq 420$ nm leads to additional weak, high-energy emission with a maximum at 580 nm, and for various reasons this high-energy shoulder is attributed to impurities.[19,20] The decay of the principal emission has been monitored at several wavelengths following excitation with ≈ 10-ns laser pulses at 530 nm. In the wavelength range 640–700 nm, Ru(II)-based chromophore CT emission decayed with a constant lifetime of 330 ns in $\mathrm{CH_3CN}$

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(19) The position of the high-energy emission maximum and excitation spectrum suggest it to be some Re(I) complex. This could either be due to a case of independent emission from the Re- and Ru-based units (dual emission)[10b,h,20] or from impurities. In the present case, the emission can be observed to varying degrees in several of the samples examined and could not be totally eliminated in spite of several purification attempts. Isomerization and cleavage problems of cyano-bridged complexes could be a source.

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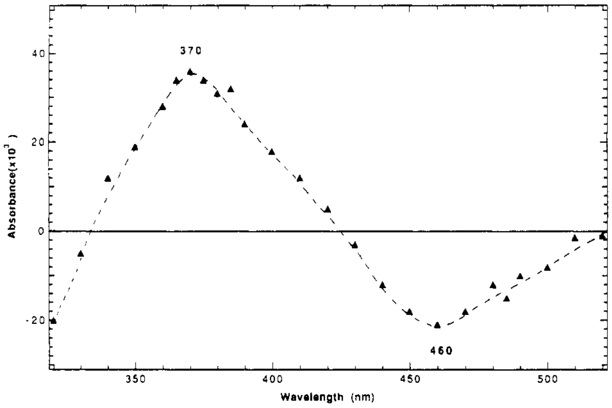

Figure 7. Transient absorption spectrum recorded during the 530-nm laser flash photolysis of complex **5** in methylene chloride (293 K). The spectrum was recorded at 50 ns following ≈10-ns laser pulse excitation.

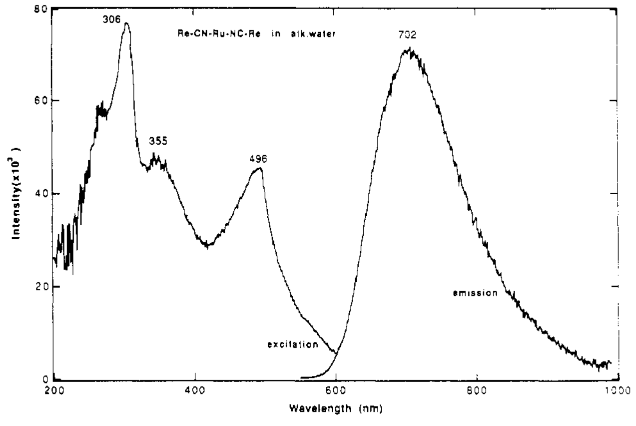

Figure 8. Emission (λ_{excit} = 500 nm) and excitation spectrum (for λ_{em} = 700 nm) of the trinuclear complex **6**, $[(bpy)(CO)_3Re–CN–Ru(bpy)_2–NC–Re(CO)_3(bpy)]^{2+}$, in alkaline water at 293 K.

(460 ns in methylene chloride, exponential, with correlation coefficient >0.98 in all cases).

The excitation spectrum obtained for the Ru-based chromophore emission ($\lambda_{em} \geq 620$ nm) is also shown in the figure. In dilute solutions ($A_{432\ nm} \leq 0.2$), the relative intensity of various absorption bands is nearly identical to that of the ground-state absorption spectrum, indicating that the intramolecular energy transfer from the Re-based chromophore to Ru-based one is very efficient. If the energy transfer had not been efficient, the excitation spectrum should show a minimum in the 350-nm region where the Re-based chromophore have their intense CT band. Reference absorption spectrum for the latter case can be found in the Rh–NC–Ru–CN–Rh complex investigated by Endicott et al. In the latter compound, the donor $[Rh(bpy)_2(CN)]$ unit has its lowest energy bands (ligand π–π^* and d–d) located at ≈310 nm.

The transient absorption spectrum following ≈10-ns laser pulse excitation of the trinuclear complex has been examined in methylene chloride at 530 nm, and this is shown in Figure 7. As mentioned earlier, 530-nm excitation leads to selective excitation of the central Ru(II)-based chromophore (eq 13). The transient spectrum obtained is typical of CT excited states in Ru(II)–polypyridyl complexes with an absorption maximum at ≈370 nm and ground-state bleaching (with its minimum at ≈460 nm). The 370-nm band is assigned to the radical anion ($bpy^{\bullet-}$) formed in the CT excitation process. The 370-nm absorption and 460-nm bleaching have an intensity ratio of roughly 1.5:1. The transient absorption and bleaching decay with a lifetime ≈450 ns, in good agreement with the CT emission measured under similar conditions.

VI. Photophysics of the Complex 6, $[Re^I–CN–Ru^{II}–NC–Re^I]^{2+}$. The absorption spectrum of the complex **6**, $[Re^I–CN–Ru^{II}–NC–Re^I]$, in alkaline aqueous solutions at room temperature is shown in Figure 5. The central Ru-based chromophore has its absorption maximum at a lower energy of 500 nm. The red-shifted nature of the lowest energy CT band of this complex is due to the relative ease of oxidation of the N-bonded Ru center. Figure 8 shows the steady-state luminescence spectrum of freshly prepared solutions of the trinuclear complex **6** (dianionic) in alkaline water. The absorption and emission spectra are solvent sensitive. In the order from ethanol to water, the lowest energy CT absorption maximum red-shifts from 492 to 500 nm and the emission from 661 to 702 nm. In fluid solutions, the emission spectral profile is independent of the excitation wavelength over the entire near-UV–visible range (350–600 nm). On the basis of the behavior of the model compounds, the weak red emission is assigned to Ru → dcbpy CT transition. The red emission from the trinuclear complex **6** is very weak ($\phi \approx 0.002$) and short-lived. In ethanol, the estimated lifetime is ≤40 ns. The photophysical and redox properties are very similar to those of the trinuclear complex $[(bpy)_2Ru–CN–Ru(dcbpy)_2–NC–Ru(bpy)_2]$ studied earlier[12,13] in connection with the sensitization of TiO_2 electrodes.

Included in Figure 8 is the excitation spectrum for the Ru-based chromophore emission monitored at 702 nm. The observed maxima and the relative intensities of various bands in the excitation spectrum are nearly identical to those in the absorption spectrum of the complex (cf. Figure 5). The absence of any emission from the Re-based chromophore and the features of the excitation spectrum indicate occurrence of efficient energy transfer from the peripheral Re units to the central Ru(II)-based chromophore.

VII. Intervalence Transitions (IT) in Partially Oxidized Species and in the CT Excited State. Partial oxidation of the multimetal centers in polynuclear complexes often give rise to intervalence transitions (IT) in the red/near-IR region. Monitoring of the IT is an elegant way or probing the extent of electronic coupling between the different metal centers. In the last two decades there have been a number of studies on the chemistry of mixed-valence compounds, particularly on the cyano-bridged systems. The intervalence transitions in cyanide-bridged systems are known to much more intense ($\epsilon_{max} \geq 3000$) than that of the corresponding aromatic polyimide-bridged complexes ($\epsilon_{max} \leq 1000$), reflecting the strong metal–metal electronic coupling in the former complexes.[12]

In order to probe the extent of electronic coupling between Re and Ru centers in the trinuclear complexes, we have examined the absorption spectra of the partially oxidized trinuclear complexes $[Re^I–NC–Ru^{II}–CN–Re^I]$ (**5**) and $[Re^I–CN–Ru^{II}–NC–Re^I]$ (**6**). Chemical oxidations were carried out either in acetonitrile and/or in 1 N H_2SO_4 using Ce(IV) as the oxidant. Figure 9 (top) shows a series of absorption spectra of complex **5** obtained during Ce(IV) oxidation in CH_3CN. Oxidation of the complex is accompanied by a growth of an IR band with a broad maximum at ≈1358 nm. On the basis of the similarity of the new absorption features with that of the partially oxidized $[Ru^{II}–CN–Ru^{III}–NC–Ru^{II}]$ complex,[12] the growing absorption in the IR region in the partially oxidized $[Re^I–NC–Ru^{III}–CN–Re^I]$ species is assigned to IT band(s). The IT absorption in the 600–1800-nm region can be fitted to a single gaussian with a maximum at 0.73 μm^{-1} (1367 nm) and bandwidth of 0.31 μm^{-1}. In the near-UV region the mixed-valence complex $[Re^I–NC–Ru^{III}–CN–Re^I]$ shows another broad maximum at 390 nm (not shown). This is a composite band containing CT transitions: bpy → Ru and Re → bpy. Isosbestic points are obtained at 592 and 400 nm up to the addition of 1 equiv of Ce(IV). The estimated molar absorbance for the IR band is ≈4000 $M^{-1}\ cm^{-1}$. The band maximum, bandwidth, and molar absorbances for the mixed-valence $[Re^I–NC–Ru^{III}–CN–Re^I]$ species are very similar to that observed for the $[Ru^{II}–CN–Ru^{III}–NC–Ru^{II}]$ species in the above cited trinuclear complex.

The 530-nm laser pulse excitation of the complex **5** in degassed acetonitrile at ambient temperature showed strong transient absorptions in the red-IR region. It may be recalled that, at this

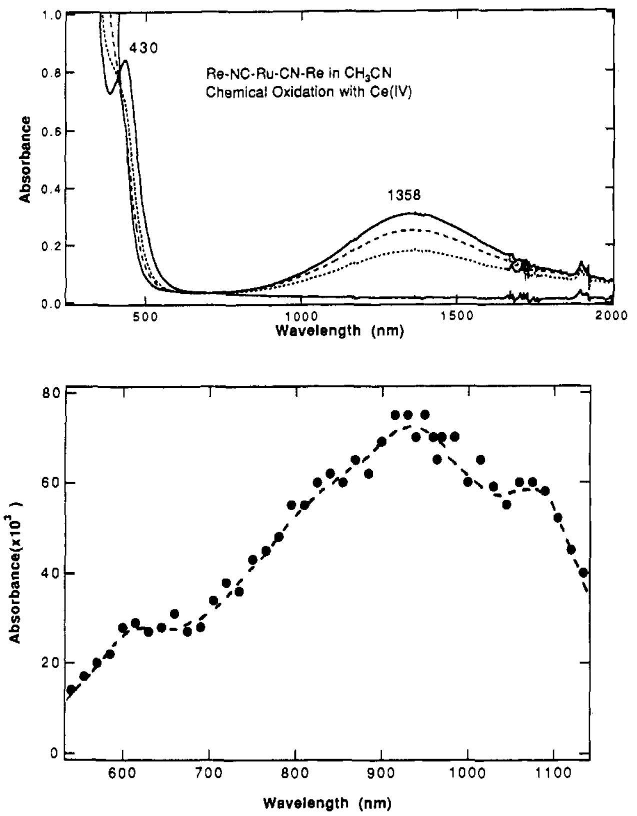

Figure 9. Top panel: Absorption spectral changes observed during Ce(IV) oxidation of complex **5** in acetonitrile. Bottom panel: Transient absorption spectrum of complex **5** in the 550–1150-nm range recorded following 530-nm laser pulse excitation in CH_3CN at 293 K.

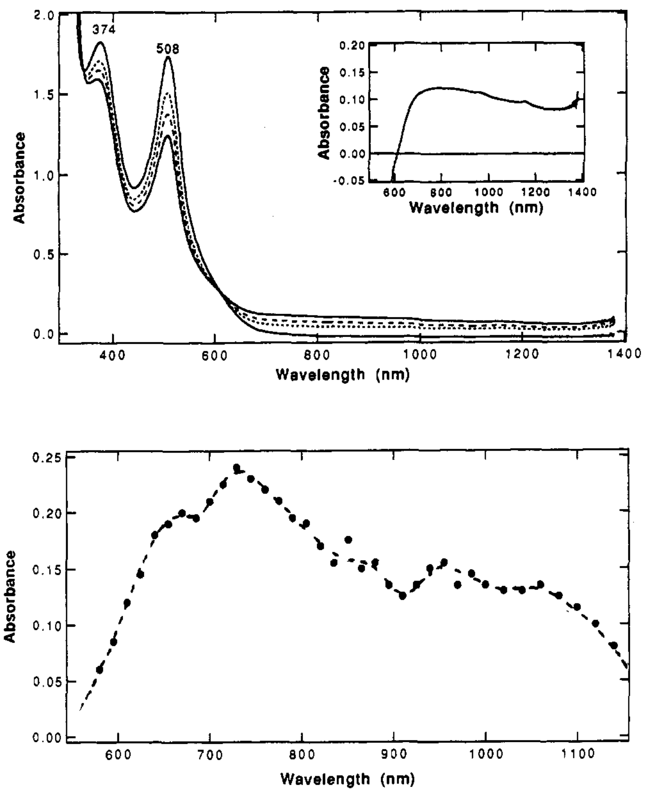

Figure 10. Top panel: Absorption spectral changes observed during Ce(IV) oxidation of complex **6** in alkaline water (pH 10). Insert: Difference absorption spectrum between the unoxidized and partially oxidized forms in acetonitrile. Bottom panel: Transient absorption spectrum of complex **6** in the 550–1150-nm range recorded following 530-nm laser pulse excitation in alkaline ethanol at 293 K.

wavelength, there is selective excitation of the central Ru chromophore. Using a EG&G photodiode (Si-based), we could measure the transient absorption changes up to 1150 nm. Figure 9 (bottom) shows the transient absorption spectrum in the 550–1150-nm range obtained in this manner. The transient absorptions in the infrared region decay exponentially with a lifetime of 330 ns, identical to the emission decay of the central Ru chromophore. The transient absorption in the red–near-IR region (≥600 nm) is assigned to intervalence transitions (IT) of mixed-valence species for the following reasons:

(i) It is well-known that excitation of polypyridyl complexes of Ru(II) to the CT excited state in effect creates an oxidized metal center (Ru^{III}) and a reduced ligand ($LL^{\bullet-}$). Thus, the trinuclear complexes with the central Ru in the CT excited state can be visualized as ***transient mixed-valence species*** as shown in eq 17. The mixed-valence species can be detected via their IT

$$[Re^I\text{-}Ru^{II}(L)_2\text{-}Re^I] \xrightarrow{h\nu} [Re^I\text{-}Ru^{II}(L)_2{}^{*}\text{-}Re^I] = [Re^I\text{-}Ru^{III}(L)(L^{-})\text{-}Re^I] \quad (17)$$

absorption only during the lifetime of the CT excited state (lifetime of Ru^{III}). Matching decay kinetics of the transient absorption of the IR band (IT) with the emission decay of CT excited state is consistent with such a description.

(ii) No such absorption in the near-IR region can be detected in the transient spectra of the parent mononuclear complex $Ru(bpy)_2(CN)_2$. Observance of intervalence (IT) transitions require, along with Ru(III), additional metal centers attached to the cyanide ligand. The situation is analogous to what is observed during chemical oxidation.

(iii) Experiments in the presence of quenchers do show that the transient absorption in the near-IR is due to a different species. In the presence of suitable electron acceptors, the transient absorptions in the IR show kinetic behavior quite different from that of the emission. Emission decay is enhanced (decay ≤ ns), but the IT band decays very slowly (several μs). Detailed studies on the application of the near-IR absorption to study mechanism of sensitization of TiO_2 electrodes are in progress, and results will be reported on a later date.

Figure 10 (top) shows the evolution of the absorption spectrum during chemical oxidation of the other **6** complex in 1 N H_2SO_4 (**6** is not soluble in acetonitrile). In the latter medium, the window available is restricted to 1380 nm. It may be recalled that, in **6**, the central Ru(II) center undergoes facile oxidation at 0.75 V. Isosbestic points are obtained at 607 and 358 nm indicating clean conversion of the [Re^I–CN–Ru^{II}–NC–Re^I] complex to the [Re^I–CN–Ru^{III}–NC–Re^I] state. In distinct contrast to the behavior observed with complex **5**, the absorption intensity of the [Re^I–CN–Ru^{III}–NC–Re^I] complex in the IR region is very weak. The insert figure shows the difference absorption spectrum between the [Re^I–CN–Ru^{III}–NC–Re^I] and [Re^I–CN–Ru^{II}–NC–Re^I] species, and it shows a broad maximum at ≈780 nm.

Figure 10 (bottom) shows the transient difference absorption spectrum recorded following 530-nm laser pulse excitation of **6** (in the [Re^I–CN–Ru^{II}–NC–Re^I] state) in alkaline ethanol. Due to the red-shifted nature of the central Ru(II) chromophore, a 532-nm laser pulse causes selective excitation of this unit. As in the chemical oxidation, formation of the CT excited state is accompanied by weak absorptions in the IR region. In both cases the IR absorption is attributed to formation of mixed-valence species and associated intervalence transitions involving central Ru(III) and peripheral Re(I) units. As in complex **5**, the transient absorption spectrum of the excited state is slightly blue-shifted with respect to the absorption spectrum of the chemically oxidized species. The transient absorption decays with a lifetime of ~35 ns, nearly identical to the emission decay of the central Ru(II) unit in the same solvent.

As per the Hush model, for mixed-valence systems with similar inner- and outer-sphere reorganization energies, the energy of the IT (E_{op}) should increase with increasing $\Delta E_{1/2}$ (difference in the oxidation potential of the two metal centers).[21] As per the data presented in Table III, $\Delta E_{1/2}$ in the oxidation potentials of the Re and Ru centers is $\approx$0.65 V for complex **6** and $\approx$0.35 V for complex **5**. The higher $\Delta E_{1/2}$ value of complex **6** with respect to **5** is reflected in the higher energy of the IT band of the former. Interestingly, (coincidence!) the $\Delta E_{1/2}$ value of complex **5** is similar to that observed for the homotrinuclear complexes of Ru, [Ru–CN–Ru–NC–Ru], and the IT maxima observed in the two cases are very similar ($\approx$0.7 μm^{-1}). The IT maximum of the complex with central Ru having cyanides C-bonded, [Ru–NC–Ru–CN–Ru], is much higher, $\approx$1.0 μm^{-1} (unpublished observations in this laboratory).

In the transient mixed-valence species formed during the lifetime of the CT excited state, the presence of the electron in one of the polypyridine ligand attaches to the Ru(III) center undergoing the intervalence process would raise the energy of the IT. Thus, the transient IT band is expected to be blue-shifted with respect to the mixed-valence species without the reduced ligand, viz., [Re^{I}–Ru^{III}(L)–Re^{I}], as has been observed. The 930-nm (1.08 μm^{-1}) maximum observed in the transient absorption spectrum indicates the energy of the IT in the excited state of complex **5** to be $\approx$1.33 eV. This compares to $\approx$0.9 eV (0.74 μm^{-1}) estimate for the energy of the IT band in the chemically oxidized species ($\approx$0.74 μm^{-1} $\approx$0.91 eV). An equivalent way of rationalizing the blue-shifted IT band in the excited state is as follows. The redox potential of the central chromophore in the excited state, E(Ru$^{II*/III}$) is 0.72 V as compared with 1.00 V for the ground state. Thus, $\Delta E_{1/2}$ increases by 0.28 V upon optical excitation and the accompanying IT band blue shifts. The difference in the energy of the IT is similar to the difference in the ground- and excited-state oxidation potential of the central Ru-based chromophore.

VIII. Dynamics of the Excited-State Decay and Intramolecular Interactions. The present study examined the photophysical and redox properties of the CT transitions of Ru(II) and Re(I) in polynuclear complexes linked by cyanide ligand(s). Major interest in complexes of this kind is on their use as light harvesting devices. The light harvesting process in the present case would involve efficient channeling of high-energy photons via transfer of the excitation energy from the peripheral Re-based units to the central Ru-based CT excited state (eq 15). Under suitable circumstances, the donor and the acceptor excited states can also undergo efficient quenching due to electron-transfer reactions of the type shown in eqs 18 and 19. These involve oxidative quenching of the excited state, and one can have reductive quenching pathways as well. In sensitizers designed as light harvesting systems, electron-transfer pathways are undesirable and must be suppressed.

$$[\text{Re–Ru–Re}] \xrightarrow{h\nu} [\textit{Re}^{*}\text{–Ru–Re}] \xrightarrow{e^{-}\,\text{tr}} [\text{Re}^{II}\text{–Ru}^{I}\text{–Re}] \quad (18)$$

$$[\text{Re–Ru–Re}] \xrightarrow{h\nu} [\text{Re–}\textit{Ru}^{*}\text{–Re}] \xrightarrow{e^{-}\,\text{tr}} [\text{Re}^{0}\text{–Ru}^{III}\text{–Re}] \quad (19)$$

In addition to the intramolecular energy- and electron-transfer pathways mentioned above, one or more of the following factors can also contribute to the observed emission lifetime for the Re(I)–bpy, Ru(II)–bpy based CT excited states in trinuclear complexes: (i) decrease in lifetime with decreasing energy of the CT excited state (energy gap law); (ii) decrease in lifetime due to reduced energy gap between the emitting CT state and upper dd state (activated deactivation pathway); (iii) spin–orbit coupling effects due to the presence of a heavy atom (can cause further weakening of the spin-forbidden nature of the electronic transitions).

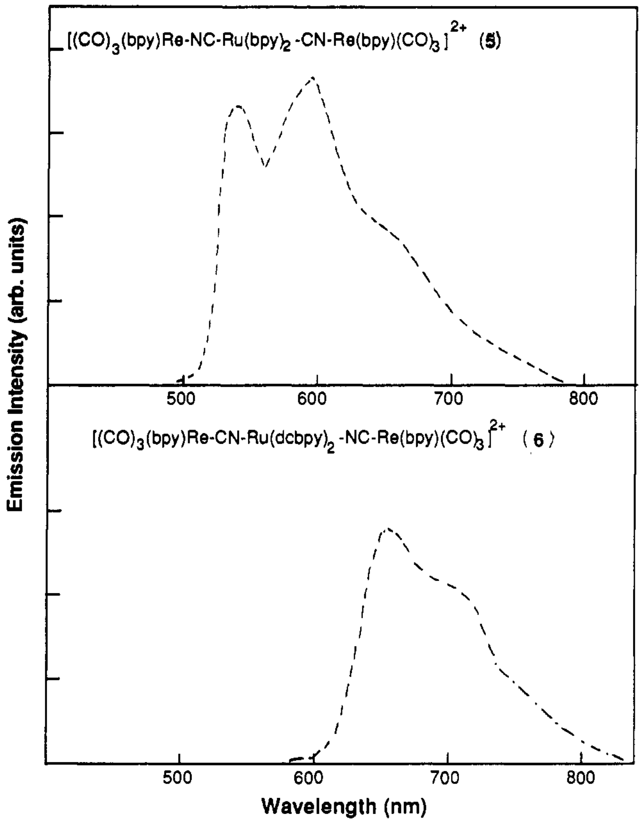

Figure 11. Top panel: Emission spectrum of trinuclear complex **5**, [(bpy)(CO)$_3$Re–NC–Ru(bpy)$_2$–CN–Re(CO)$_3$(bpy)]$^{2+}$ in ethanol–methanol (4:1 v/v) at 77 K (λ_{excit} = 430 nm). Bottom panel: Emission spectrum of **6**, [(bpy)(CO)$_3$Re–CN–Ru(dcbpy)$_2$–NC–Re(CO)$_3$(bpy)]$^{2+}$, in ethanol–methanol (4:1 v/v) at 77 K (λ_{excit} = 490 nm).

Feasibility of occurrence of these processes can be assessed from a thermodynamic analysis of the energies and redox potentials of the relevant ground and excited states. Ground-state redox potentials and excited-state energies can be used in the following relations to obtain estimates of the excited-state redox potentials:

$$E(\text{M}^{+}/\text{M}^{*}) = E(\text{M}^{+}/\text{M}) - E^{*} \qquad (20)$$

$$E(\text{M}^{*}/\text{M}^{-}) = E(\text{M}/\text{M}^{-}) + E^{*} \qquad (21)$$

The procedure requires precise information on the zero–zero spectroscopic energy of the excited state (E^{*}) and the assumption that the differences in the entropic terms between the ground and excited state are negligible. Best estimates of the excited-state energy E^{*} are obtained from the onset values of the emission in a low-temperature matrix (ethanol–methanol glass at 77 K for example).

Figure 11 (top panel) shows the emission from the Ru-based chromophore of complex **5** observed in ethanol–methanol glass (4:1 v/v) at 77 K. The emission spectrum consists of fairly well-resolved maxima at 542 and 602 nm. The lifetime for the Ru-bpy CT emission has been determined to be 4.09 μs (353-nm excitation). The observed emission maximum for the CT excited state of the central C-bonded Ru chromophore (542 nm) is very similar to that observed for similar C-bonded Ru(bpy)$_2$ units in Rh–NC–Ru–CN–Rh[14] and Pt–NC–Ru–CN–Pt[11c] trinuclear complexes. Figure 11 (bottom) shows the emission spectrum of **6** measured in ethanol–methanol glass (4:1 v/v) at 77 K for λ_{excit} = 450 nm. At this wavelength there is selective excitation of the central Ru-based chromophore, and the emission maximum is at 655 nm. The CT emission of the central N-bonded Ru(II) unit is slightly blue-shifted with respect to emission from similar Ru(II) unit in the homotrinuclear complex, (NC)Ru–CN–Ru–NC–Ru(CN). In alcoholic glass, the latter has its emission maximum located at 684 nm.

In mononuclear transition metal polypyridyl complexes, the excited state redox potentials can be calculated fairly precisely

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(21) (a) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557; *Prog. Inorg. Chem.* **1967**, *8*, 391; *Electrochim. Acta* **1968**, *13*, 1005. (b) Creutz, C. *Prog. Inorg. Chem.* **1988**, *30*, 1.

Table V. Estimates of Excited-State Energies and Redox Potentials of Various Re Complexes

complex	ex state	E^*(eV)	E^*_{red}(V)	E^*_{ox}(V)
$Re(CO)_3(bpy)(Cl)$ (**1**)	Re–bpy CT	2.25	+0.91	−0.92
$Re(CO)_3(bpy)(CN)$ (**3**)	Re–bpy CT	2.37	+1.00	−1.05
$[(bpy)Re–CN–Re(bpy)]^+$ (**4**)	Re–bpy CT	2.34	+1.05	−1.00
$[Re–NC–Ru–NC–Re]^{2+}$ (**5**)	Re–bpy CT	2.35	+1.12	−0.89
	Ru–bpy CT	2.29	+0.72	−1.29
$[Re–CN–RuNC–Re]^{2+}$ (**6**)	Re–bpy CT	2.35	+1.05	−0.95
	Ru–dcbpy CT	1.89	+0.65	−1.14

using the above equations and the first (one-electron) oxidation and reduction potentials and the excited-state energies. A number of useful electrochemical correlations have been noted earlier.[22,23] In ligand-bridged complexes where the electronic coupling between the different chromophoric units are strong, the above procedure can be imprecise due to practical problems in obtaining the required electrochemical data. Only the first oxidation and reduction processes involve the polynuclear complex in the ground state, and the corresponding excited state potentials are accurate. Successive electrochemical oxidation/reduction involve species that are already oxidized/reduced. Hence these potentials can only be upper estimates to the redox potentials of interest. In complex **5**, for example, the first oxidation involves the Ru(II) center and first reduction involves the bpy ligand attached to the Re(I) center. The measured second oxidation corresponds to oxidation of partially oxidized complex, viz., $[Re^I–Ru^{III}–Re^I]$, and not of the required $[Re^I–Ru^{II}–Re^I]$ species. This will give an upper limit to the required value. Same arguments hold good for the third and successive oxidation and reduction potentials measured. For these reasons, excited-state redox potential estimates made using eqs 20 and 21 and the second and successive redox potentials are upper limits and should be interpreted with care. Excited-state energies and redox potentials have been calculated for the Re, Re–Re, and Re–Ru–Re complexes, and these are presented in Table V. E^*_{red} and E^*_{ox} refer to redox potentials for the respective excited state to act as an oxidant and reductant, respectively.

Examination of the data on the excited-state energies and redox potentials presented in Tables IV and V leads to several important conclusions on possible intramolecular energy- and electron-transfer processes. Due to lower energies of the CT state of the central Ru(II) unit, intramolecular energy transfer from the CT state of peripheral Re units is feasible in both complexes **5** and **6**. The estimated energy gaps between the relevant CT excited states are 120 and 460 mV, respectively. The excitation spectra obtained for Ru-based emission in both complexes are supportive of the occurrence of energy transfer.

As regards intramolecular electron-transfer processes, the oxidation and reduction potentials of the lower energy Ru(II)-based CT excited state are not high enough for it to undergo any redox quenching (e.g. eq 16) with the terminal Re-based carbonyl polypyridyl unit. Thus, one does not expect any quenching of the emission of the Ru-based chromophore, and this indeed is observed experimentally. For the CT excited state of the peripheral Re-based chromophore, its reduction potentials are not high enough to undergo reductive quenching with the central Ru unit.

The oxidative quenching of the Re-based CT excited state by the central Ru unit cannot be ruled out in both complexes (eq 22). On the basis of the data presented in Table V, the driving force for this reaction can be estimated to be ≈100 and 300 mV for complexes **5** and **6**, respectively. The photoinduced electron-transfer reaction (22) is followed by back-electron-transfer involving the central Ru(III) and reduced bpy ligand attached to peripheral Re(I) units, giving back the starting materials.

$$[Re–Ru–Re] \xrightarrow{h\nu} [Re^*–Ru–Re] \xrightarrow{e^-\ tr} [Re^0–Ru^{III}–Re]^* \quad (22)$$

For strongly coupled systems, intramolecular electron transfer can be extremely rapid. Intervalence transitions observed in cyano-bridged complexes clearly suggest ease of electron transfer between the different fragments. It may be pointed that, in the homobinuclear and homotrinuclear cyano-bridged complexes containing $Ru(bpy)_2$ units, the partially oxidized species are known to be nonemissive. The quenching of emission from higher energy chromophores has been attributed to efficient intramolecular electron transfer. For example, in $[Ru^{II}–CN–Ru^{III}–NC–Ru^{II}]$, the electron promoted from the terminal C-bonded Ru(II) to one of its bpy ligands is transferred subsequently to nearby N-bonded Ru(III). The quenching of emission from the higher energy chromophore (C-bonded Ru) can also occur in the nonoxidized $[Ru^{II}–CN–Ru^{II}–NC–Ru^{II}]$ by hole transfer mechanisms of the type shown in the scheme above. In 4,4′-bpy- or pyrazine-bridged polypyridyl complexes of Ru(II), Os(II), or Re(I), evidence has been found[24] for the occurrence of intramolecular electron/hole transfer following production of a localized CT excited state.

In complex **6**, the larger driving force for the energy transfer indicates this to be the preferred mechanism over electron transfer. Intramolecular energy transfer from the tricarbonyl(polypyridine)Re(I) unit to the Ru(II)–polypyridyl unit has been reported recently in the binuclear complex $[(bpy)_2Ru–bpyen–Re(CO)_3(py)]^{3+}$.[3,10b] In this complex the donor and acceptor are connected by a flexible methylene spacer. The ground-state absorption spectrum of the binuclear complex is a sum of the constituent D,A units, and there is only very weak electronic coupling between the D,A chromophores.

Intramolecular energy-transfer processes can be studied directly by monitoring the growth of the acceptor luminescence (in this case central Ru(II)-based CT excited state) for different excitation wavelengths, specifically at those wavelengths where there is preferential excitation of the donor chromophore. Population of the acceptor excited state by intramolecular energy transfer will give rise to growth of the emission intensity in addition to those formed immediately by direct excitation. Earlier studies on $[Ru^{II}–CN–Cr^{III}]$ and $[Ru^{II}–CN–Rh^{III}]$ systems indicate that this process to be rapid, occurring "on a time scale shorter than a few nanoseconds". Establishment of intramolecular electron transfer would require detailed analysis of the transient absorption over a wide wavelength and time scale. Unlike luminescence where emission from the acceptor can be monitored separately, in transient spectral studies there is extensive overlap of the absorption spectra of the excited states and relevant redox intermediates render quantitative analysis complex. Precise information on the spectra of the excited states and products is difficult to obtain without resorting to various assumptions.

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