

Ligand-bridged Homo- and Hetero-binuclear Carbonyl Polypyridyl Complexes of Re^I: Syntheses, Electronic Spectra, Redox, and Luminescence Behaviour

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Electronic absorption data, redox potentials, and photophysical properties are reported for a series of mono- and ligand-bridged bi-nuclear carbonyl polypyridyl complexes of Re^I: [$\{\text{ReCl}(\text{CO})_3\}_n\text{L}^b$] and $[(\text{OC})_3\text{ClRe}(\text{L}^b)\text{M}(\text{bipy})_2]^{2+}$ [bridging ligand (L^b) = 2,3-bis(2'-pyridyl)pyrazine (dpp) or 2,3-bis(2'-pyridyl)quinoxaline(dpq); bipy = 2,2'-bipyridine; M = Ru^{II} or Os^{II}; $n = 1$ or 2]. For all the binuclear complexes examined, electronic absorption and electrochemical data indicate extensive stabilization of the ligand π^* orbital upon binucleation. These are also the first cases of strongly coupled ligand-bridged dimeric complexes of Re^I that exhibit luminescence (charge-transfer type) in solution at room temperature. Data on the emission maxima and lifetimes of heterobinuclear complexes of Re and Ru confirm earlier indications that the emitting state is essentially localized on the Ru \rightarrow L^b charge transfer.

The Taube–Creutz ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ represents a classical example of a ligand-bridged binuclear complex. Since its introduction two decades ago,¹ a number of such ligand-bridged complexes have been made with numerous ligand bridges (L^b)† of intriguing structure, symmetry/stereochemistry. Complexes have been prepared with identical or different metal centres (identified hereafter as ‘homo’ or ‘hetero’ respectively) and also with similar or dissimilar spectator ligands (L^s) (identified hereafter as ‘symmetric’ or ‘asymmetric’). The majority of these studies have been on complexes with the two metal centres in different oxidation states and consequently devoted to various aspects of ‘mixed-valence ion’ chemistry.^{2–7}

Ligand-bridged polynuclear complexes are interesting candidates to examine interchromophore interactions and light-induced multi-electron transfer processes. Knowledge of the photophysical and redox properties is essential for a proper assessment of their photoredox behaviour. Luminescence, though not a requisite, does help direct monitoring of excited-state reactions. In this context, studies devoted to the characterization of the excited-state photophysics in polynuclear, polypyridyl complexes are few in number and interest has been shown only recently.⁸ Metal complexes with polypyridyl ligands are ideal candidates for detailed scrutiny due to their rich, diverse photophysics and photoredox activity.

Of particular relevance to the work reported here are the studies that have been made on: (a) homo- and hetero-binuclear polypyridyl complexes of the type $[\text{L}^s_2\text{M}^1(\text{L}^b)\text{M}^2\text{L}^s_2]$ ($\text{M}^1, \text{M}^2 = \text{Ru}$ or Os);^{9–19} (b) homo- and hetero-binuclear carbonyl polypyridyl complexes of the type $[(\text{OC})_n\text{M}^1(\text{L}^b)\text{M}^2(\text{CO})_n]$, $n = 4$ or 5 ; $\text{M}^1, \text{M}^2 = \text{Mo}, \text{Cr},$ or W ;^{20–27} and (c) heterobinuclear carbonyl polypyridyl complexes of the type $[(\text{OC})_3\text{ClM}^1(\text{L}^b)\text{M}^2\text{L}^s_2]$ ($\text{M}^1 = \text{Re}, \text{M}^2 = \text{Ru}$).^{28–31} As in complexes composed entirely of polypyridyl ligands, in all of the carbonyl polypyridyl complexes the lowest excited state is also of $\text{M} \rightarrow \text{L}^b$ charge-transfer (c.t.) type. Cases have been identified where the two metal centres remain unperturbed, weakly perturbed, or strongly perturbed. Electronic absorption, redox, and luminescence properties are useful guides to such classification. Non-interacting complexes display properties reflecting a composite of mononuclear fragments. Moderate or strong coupling between the metal centres leads to spectral shifts in absorption, emission, and very different redox potentials as compared to monomeric chromophores.

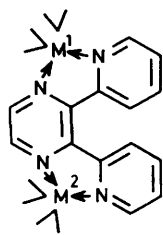
As an example under categories (b) and (c), Vogler and Kisslinger²⁸ examined the absorption and luminescence of the homodimer $[\{\text{ReCl}(\text{CO})_3\}_2(\text{bpym})]$ [abbreviated as $\text{Re}(\text{bpym})\text{Re}$] and the heterodimer $[(\text{OC})_3\text{ClRe}(\text{bpym})\text{Ru}(\text{bipy})_2]^{2+}$ [abbreviated as $\text{Re}(\text{bpym})\text{Ru}$] and reported some interesting observations: (i) the mononuclear rhenium(I) complex was luminescent in solution at room temperature but the homo $\text{Re}(\text{bpym})\text{Re}$ dimer was non-luminescent even as a solid at 77 K; (ii) the emission from the solid sample of the hetero $\text{Re}(\text{bpym})\text{Ru}$ dimer resembled that of the homo $\text{Ru}(\text{bpym})\text{Ru}$ dimer. These observations have been confirmed recently by Juris *et al.*²⁹ who also reported on an emissive binuclear rhenium complex, $[\{\text{ReCl}(\text{CO})_3\}_2(\text{tmqpy})]$. Close resemblance of the absorption, emission, and redox properties of this complex with those of monomeric fragments strongly suggests that the two fragments are non-interacting. During the preparation of this manuscript, two other related papers have appeared. Rillema and co-workers³⁰ reported on the syntheses of some highly luminescent polynuclear rhenium complexes, e.g. $[(\text{bipy})\text{Ru}\{\text{bpym}\}\text{ReCl}(\text{CO})_3]^{2+}$ and $[(\text{bipy})_2\text{Ru}(\text{dpzq})\{\text{ReCl}(\text{CO})_3\}_2]^{2+}$. Meyer and co-workers³¹ have described elegant intramolecular energy transfer in 4,4'-bipy bridged complexes of the type $[\{\text{Re}(\text{CO})_3\text{L}^s\}_2\text{L}^b]$. In these complexes, with appropriate choice of spectator ligand L^s and the solvent, it is possible to tune the nature of the lowest excited state (from $\text{Re} \rightarrow \text{L}^b$ to $\text{Re} \rightarrow \text{L}^s$ c.t.).

Herein we report an extended study of a series of homo- and hetero-binuclear carbonyl polypyridyl complexes of Re^I using dpp (1) or dpq (2) as bridging ligands to verify the above intriguing observations. Data are presented on the electronic absorption, redox potentials, and emission (spectra and lifetimes). While confirming the earlier observation of Vogler that in the hetero Ru–Re dimers the lowest excited state is of Ru \rightarrow bipy c.t. type, herein we report the first example of a luminescent strongly coupled Re–Re homodimer. In some respects, the present studies on ligand-bridged dimers of Re^I

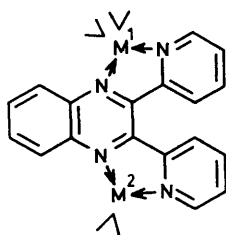
† Ligand abbreviations used, L^b, L^s refer to polypyridyl ligands of the bridging and non-bridging (spectator) type respectively; pyz = pyrazine; bpym = 2,2'-bipyrimidine; dpp = 2,3-bis(2'-pyridyl)pyrazine; dpq = 2,3-bis(2'-pyridyl)quinoxaline; tmqpy = 5,5',3'',5'''-tetramethyl-2,2':6'2'':6'',2'''-quaterpyridine; dpzq = dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline; bipy = 2,2'-bipyridine.

Table 1. Data on the elemental analyses of rhenium complexes with calculated values in parentheses

Complex	Colour	Yield (%)	Analysis (%)			
			C	H	N	Cl
[ReCl(CO) ₃ (dpp)]	Brick-red	63	37.35 (37.80)	1.90 (1.85)	10.45 (10.40)	6.80 (6.55)
[ReCl(CO) ₃ (dpq)]	Bright red	60	42.35 (42.90)	2.00 (1.70)	9.50 (9.55)	6.00 (6.05)
[(OC) ₃ ClRe(dpp)ReCl(CO) ₃]	Dark red	67	28.45 (28.40)	1.30 (1.20)	6.55 (6.65)	8.20 (8.40)
[(OC) ₃ ClRe(dpp)Ru(bipy) ₂][PF ₆] ₂ ·5H ₂ O	Deep violet	79	33.40 (33.55)	1.95 (2.15)	7.95 (8.45)	2.65 (2.65)
[(OC) ₃ ClRe(dpp)Os(bipy) ₂][PF ₆] ₂ ·6H ₂ O	Deep violet	73	31.00 (31.00)	2.00 (2.10)	7.80 (7.80)	2.60 (2.35)
[(OC) ₃ ClRe(dpq)ReCl(CO) ₃] ₂ ·4H ₂ O	Black	66	29.45 (29.85)	1.45 (1.85)	5.70 (5.80)	7.35 (7.35)
[(OC) ₃ ClRe(dpq)Ru(bipy) ₂][PF ₆] ₂ ·6H ₂ O	Black	70	34.35 (35.20)	2.50 (2.75)	8.05 (8.00)	2.75 (2.55)
[(OC) ₃ ClRe(dpq)Os(bipy) ₂][PF ₆] ₂ ·5H ₂ O	Black	65	32.60 (33.50)	2.60 (2.45)	7.05 (7.60)	2.30 (2.40)
[Os(bipy) ₂ (dpq)][PF ₆] ₂	Deep violet	70	42.80 (42.45)	2.80 (2.45)	10.60 (10.45)	



M¹(dpp)M²
(1)



M¹(dpq)M²
(2)

complement studies on the metal-metal bonded carbonyl polypyridyl complexes of type [(OC)₅Re-Re(CO)₃(L^b)].^{32,33}

Experimental

Materials.—The complex [ReCl(CO)₅] was obtained from Pressure Chemicals and used without further purification. The ligands 2,3-bis(2'-pyridyl)pyrazine (dpp) and 2,2'-bipyrimidine (bpym) were from Alfa Inorganics and were used as supplied. 2,3-bis(2'-pyridyl)quinoxaline (dpq) was prepared from 2,2'-pyridil and *o*-phenylenediamine using the procedure of Goodwin and Lions.³⁴

Synthesis.—*Mononuclear rhenium(I) complexes.* The complexes [ReCl(CO)₃L^b] (L^b = dpp, bpym, or dpq) were prepared by treating stoichiometric quantities (mmol dm⁻³) of [ReCl(CO)₅] and the ligand L^b in toluene under reflux for 1 h.^{35,36} The product precipitated from solution upon cooling. It was filtered off, washed with iso-octane, diethyl ether, and air-dried. The complexes were further purified on a Woelm silica gel column using methylene chloride as eluant.

Binuclear rhenium(I) complexes. The complexes [{ReCl(CO)₃}]₂L^b (L^b = dpp, bpym, or dpq) were prepared by sequential chelation of the mononuclear complex [ReCl(CO)₃L^b] with [ReCl(CO)₅] (latter in three-fold excess), again in toluene under reflux for 1 h. Heterobinuclear complexes [(OC)₃ClRe(L^b)M(bipy)₂][PF₆]₂ (L^b = dpp, bpym, or dpq; M = Ru^{II} or Os^{II}) were prepared by treating [M(bipy)₂(L^b)]⁺[PF₆]₂⁻ with [ReCl(CO)₅] (latter in three-fold excess) in

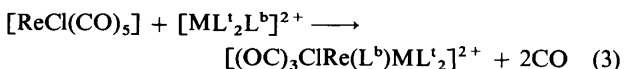
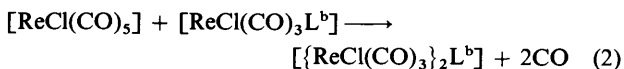
ethanol under reflux for *ca.* 4 h. In both cases, the solvent was removed under reduced pressure, the product repeatedly washed with iso-octane and ether {removes excess of [ReCl(CO)₅]}, and used without further purification. Yields of the mono- and bi-nuclear complexes are typically in the range of 60–80%.

Heterobinuclear complexes were recrystallized as hydrates. Satisfactory elemental analyses were obtained for all of the new complexes synthesized in this work. Data on the colour, yields, and elemental analyses of various complexes are presented in Table 1. Absorption spectral features of various homo- and hetero-binuclear complexes are presented and discussed in the Results and Discussion section.

Methods.—Absorption spectra were recorded on a Cary 210 spectrophotometer. Room-temperature emission spectra were recorded on a Spex Fluorolog spectrofluorimeter and were corrected for variation in the lamp output and detector (Hamamatsu R928) response. Low-temperature emission spectra were recorded on a Hitachi Perkin-Elmer MPF4F spectrofluorimeter, also fitted with a Hamamatsu R928 photomultiplier tube. Emission lifetimes were determined on a nanosecond laser flash photolysis set-up using either the 353-nm (for mononuclear rhenium complexes) or 530-nm (for binuclear complexes) laser pulses from a Q-switched Nd-YAG laser. Based on the variations in different sample preparations, estimated errors in reported values are ±4 nm in absorption, emission maxima and ±20% in emission lifetimes.

Results and Discussion

Synthesis and Stability of Complexes in Solution.—The mono- and bi-nuclear rhenium(I) carbonyl polypyridyl complexes were prepared *via* a sequential chelation procedure, using [ReCl(CO)₅] and appropriate ligand/mononuclear precursor complex [reactions (1)–(3)]. Reactions (1) and (2) have been



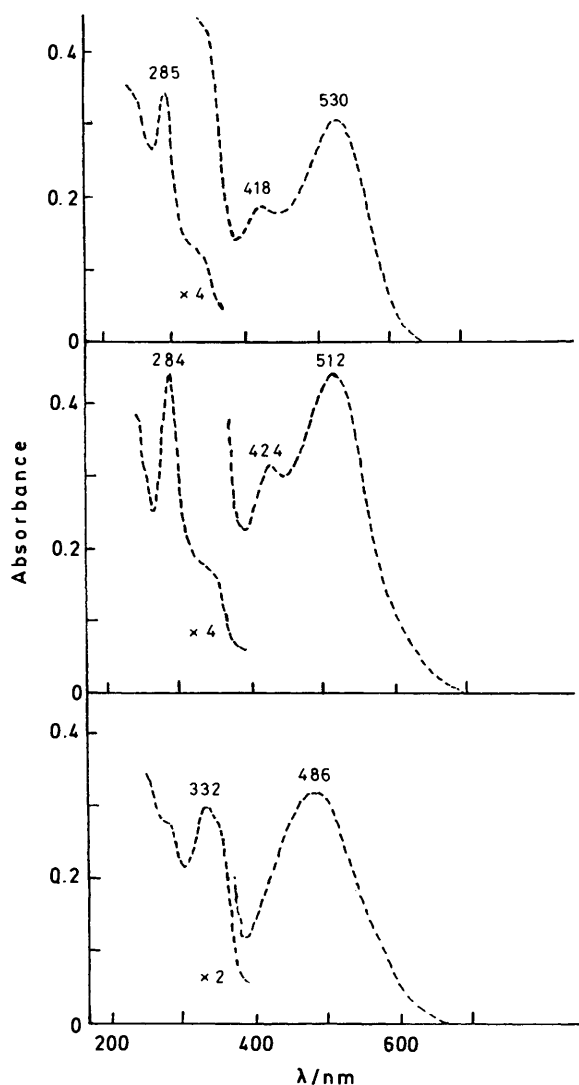


Figure. Absorption spectra of binuclear rhenium(I) complexes in methylene chloride: $[\{\text{ReCl}(\text{CO})_3\}_2(\text{dpp})]$ (bottom), $[(\text{OC})_3\text{ClRe}(\text{dpp})\text{Ru}(\text{bipy})_2]^{2+}$ (middle), and $[(\text{OC})_3\text{ClRe}(\text{dpp})\text{Os}(\text{bipy})_2]^{2+}$ (top)

carried out in toluene and (3) in ethanol, all under short reflux (1–2 h) and using a three-fold excess of $[\text{ReCl}(\text{CO})_5]$ to assure quantitative insertion. Excess of $[\text{ReCl}(\text{CO})_5]$ was removed by repeated washings with iso-octane and ether, and the complexes were purified on a silica column wherever necessary.

In non-polar solvents such as methylene chloride all the mono- and bi-nuclear complexes were quite stable. However, in polar solvents such as acetonitrile or water the binuclear complexes undergo slow cleavage to the mononuclear fragments, as indicated by (i) absorption spectral changes with time and (ii) growth of a new luminescence, characteristic of the mononuclear precursor complex of reaction (2) or (3). As the luminescence of the mononuclear precursor complex is more intense than that of the binuclear complex, luminescence serves as a very sensitive monitor of this cleavage process. Hence most of the studies reported in this work are restricted to methylene chloride as the solvent.

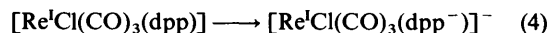
Electronic Absorption Spectra.—The Figure presents representative absorption spectra for some of the binuclear rhenium(I) complexes $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^b)]$ and $[(\text{OC})_3\text{ClRe}(\text{L}^b)\text{ML}'_2]^{2+}$ examined in this work. Table 2 summarizes data on the absorption maxima (along with molar absorption

coefficients) for various mono- and bi-nuclear complexes prepared in this work. Several mononuclear rhenium(I) carbonyl polypyridyl complexes have been prepared earlier and their absorption and luminescence characterized.^{35,36} The lowest-energy band is assigned to the metal-to-ligand charge transfer (m.l.c.t.) $[\text{Re} \rightarrow \text{L}^b(\pi^*)]$ and ligand-localized (π, π^*) bands are located in the u.v. region. The lowest-energy absorption bands of mononuclear dpp and dpq complexes are red-shifted relative to that of the bipy complex by 40–60 nm. Such red shifts are consistent with the ease of reduction of these bridging ligands (*cf.* electrochemical data for these complexes presented below).

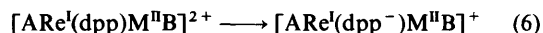
For the binuclear complexes the lowest-energy absorption band further red-shifts by 60–80 nm, relative to that of the mononuclear rhenium(I) complex. Such red shifts are reminiscent of similar behaviour observed in the binuclear complexes of Ru^{II} and Os^{II} with these ligands $[\text{Ru}(\text{L}^b)\text{Ru}]$ and $[\text{Os}(\text{L}^b)\text{Os}]$ reported earlier^{9–16} and also with the absorption spectral shifts observed in the bipy-bridged complexes of Re .¹⁰ Thus, as regards the through-ligand communications between the two metal centres, all the binuclear complexes of Re^{I} prepared in this work belong to the ‘strongly coupled’ case.

For various binuclear dpp and dpq complexes, with a given bridging ligand, the lowest-energy absorption (m.l.c.t.) band follows the order: $\text{Re-Re} > \text{Re-Ru} > \text{Re-Os} \geq \text{Ru-Ru} > \text{Ru-Os} > \text{Os-Os}$. For the heterobinuclear complexes, one can clearly distinguish two maxima in the visible region. The higher-energy one occurs at wavelengths very similar to M-L^b bands (*ca.* 420 ± 10 nm) of the mononuclear $[\text{M}^{\text{II}}\text{L}'_2\text{L}^b]^{2+}$ complexes and hence is assigned to the $\text{M} \rightarrow \text{L}^b$ c.t. transition. The lower-energy band can arise in principle from $\text{Re} \rightarrow \text{L}^b$ c.t. absorption or from $\text{M}^{\text{II}} \rightarrow \text{L}^b$ c.t. absorption. The longer-wavelength location of the band maxima as compared to the calculated mean for the corresponding homodimers suggests that the c.t. transitions associated with $\text{M}^{\text{II}} \rightarrow \text{L}^b$ are lower in energy as compared to $\text{Re} \rightarrow \text{L}^b$ c.t. transitions. In such cases, one can expect the luminescence to be dominated by the M^{II} -based chromophore and not by the Re -based chromophore. As will be shown later, this hypothesis is verified experimentally.

Electrochemistry.—Electrochemical measurements of redox potentials are instructive as they allow assignment of the lowest c.t. excited state. Redox potentials for successive one-electron reduction and oxidation of various rhenium complexes have been determined in methylene chloride and results are presented in Table 3 together with tentative assignments. One-electron reduction of the mononuclear complex $[\text{Re}^{\text{I}}\text{Cl}(\text{CO})_3(\text{dpp})]$ occurs at -1.05 V (*vs.* saturated calomel electrode, *s.c.e.*). The similarity of this value to that observed for other monomeric dpp complexes such as $[\text{Ru}(\text{bipy})_2(\text{dpp})]^{2+}$ (ref. 11) and $[\text{Os}(\text{bipy})_2(\text{dpp})]^{2+}$ (ref. 14) suggests that this reduction wave is associated with the ligand dpp [equation (4)]. For the binuclear



complexes, $\text{ARe}(\text{dpp})\text{ReA}$, $\text{ARe}(\text{dpp})\text{RuB}$, and $\text{ARe}(\text{dpp})\text{OsB}$, [where A and B represent the ligands $\text{Cl}(\text{CO})_3$ and $(\text{bipy})_2$ respectively], this first reduction (bridging ligand dpp-based) is anodically shifted by *ca.* 300 mV and occurs at $\approx -0.70 \pm 0.05$ V (*vs.* *s.c.e.*) equations (5) and (6). The anodic shift and its



magnitude upon binucleation in rhenium complexes is similar to that observed earlier^{9–15} for binucleation in homo- and hetero-binuclear dpp complexes involving Ru and Os.

Table 2. Absorption spectral data for homo- and hetero-binuclear ligand-bridged complexes of Re^I, Ru^{II}, and Os^{II} in methylene chloride

Complex ^a	Absorption (λ_{\max}/nm ($10^3\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$))			Ref. ^b
	M→L ^b c.t.	M→L ^I c.t.	π, π^*	
Mononuclear complexes				
[ReCl(CO) ₃ (dpp)]	418 (3.06)		318 (9.95)	t.w.
[ReCl(CO) ₃ (dpq)]	446 (3.23)		370 (9.89)	268 (25.5) t.w.
[ReCl(CO) ₃ (bipy)]	386 (3.45)		292 (15.9)	35
[ReCl(CO) ₃ (bpym)]	384 (2.70)		310 (sh)	232 (23.0) 28, 29
Binuclear complexes				
ARe(dpp)ReA	486 (6.32)		334 (9.98)	274 (8.48) t.w.
ARe(dpp)RuB ²⁺	512 (9.57)	424 (6.49)	324 (14.62)	282 (32.1) t.w.
ARe(dpp)OsB ²⁺	530 (9.70)	418 (6.21)	334 (13.98)	285 (31.6) t.w.
ARe(dpq)ReA	528 (4.86)	398 (7.83)	318 (14.6)	288 (11.0) t.w.
ARe(dpq)RuB ²⁺	580 (8.82)	474, 402 (16.6)	338 (20.0)	295 (60.4) t.w.
ARe(dpq)OsB ²⁺	596 (12.12)	404 (14.94)	389 (13.5)	289 (46.2) t.w.
ARe(bpym)ReA	480 (3.7)		350 (6.60)	28, 29
ARe(bpym)RuB ²⁺	558 (4.50)	414 (16.0)	284 (44.0)	243 (35.0) 28, 29

^a In binuclear complexes the spectator ligands Cl(CO)₃ and (bipy)₂ are simply denoted as A or B respectively, e.g. ReCl(CO)₃ as ReA, Ru(bipy)₂ as RuB, and Os(bipy)₂ as OsB. ^b t.w. = This work.

Table 3. Redox potentials of homo- and hetero-binuclear ligand-bridged rhenium(I) complexes measured in methylene chloride with NBu₄ClO₄ as support electrolyte, in volts vs. s.c.e. (^{a,b} as in Table 2).

Complex ^a	$E_1(\text{red})$			$E_2(\text{ox})$		Ref. ^b
	(1)	Assignment	(2)	(1)	Assignment	
dpp Complexes						
[ReCl(CO) ₃ (dpp)]	-1.05	(dpp)		1.33	Re ^I → Re ^{II}	t.w.
[Ru(bipy) ₂ (dpp)] ²⁺	-1.14	(dpp)	-1.53	1.34	Ru ^{II} → Ru ^{III}	11, 14, 15
[Os(bipy) ₂ (dpp)] ²⁺	-1.05	(dpp)	-1.39	0.85	Os ^{II} → Os ^{III}	11, 14, 15
ARe(dpp)ReA	-0.69	(dpp)	-0.97	> 1.4	Re ^I → Re ^{II}	t.w.
ARe(dpp)RuB ²⁺	-0.66	(dpp)	-1.20	> 1.34	Re ^I → Re ^{II}	t.w.
ARe(dpp)OsB ²⁺	-0.74	(dpp)		1.10	Os ^{II} → Os ^{III}	t.w.
BRu(dpp)RuB ⁴⁺	-0.71	(dpp)	-1.18	1.33	Ru ^{II} → Ru ^{III}	11, 14, 15
BRu(dpp)OsB ⁴⁺	-0.73	(dpp)	-1.13	0.90	Os ^{II} → Os ^{III}	11, 14, 15
BOS(dpp)OsB ⁴⁺	-0.72	(dpp)	-1.10	0.83	Os ^{II} → Os ^{III}	11, 14, 15
dpq Complexes						
[ReCl(CO) ₃ (dpq)]	-0.83	(dpq)	-1.33	> 1.5	Re ^I → Re ^{II}	t.w.
[Ru(bipy) ₂ (dpq)] ²⁺	-0.78	(dpq)	-1.45	1.39	Ru ^{II} → Ru ^{III}	16
[Os(bipy) ₂ (dpq)] ²⁺	-0.72	(dpq)	-1.39	1.07	Os ^{II} → Os ^{III}	t.w.
ARe(dpq)ReA	-0.33	(dpq)	-1.13	> 1.30	Re ^I → Re ^{II}	t.w.
ARe(dpq)RuB ²⁺	-0.30	(dpq)	-0.91	> 1.36	Re ^I → Re ^{II}	t.w.
ARe(dpq)OsB ²⁺	-0.30	(dpq)	-0.88	1.17	Os ^{II} → Os ^{III?}	t.w.
BRu(dpq)RuB ⁴⁺	-0.37	(dpq)	-1.10	1.47	Ru ^{II} → Ru ^{III}	16
bpym complexes						
[ReCl(CO) ₃ (bpym)]	-1.03	(bpym)	-1.65	1.43	Re ^I → Re ^{II}	28, 29
[Ru(bipy) ₂ (bpym)] ²⁺	-1.01	(bpym)	-1.45	1.40	Ru ^{II} → Ru ^{III}	28, 29
ARe(bpym)ReA	-0.51	(bpym)	-1.20	1.48	Re ^I → Re ^{II}	28, 29
BRu(bpym)RuB ⁴⁺	-0.41	(bpym)	-1.08	1.53	Ru ^{II} → Ru ^{III}	28, 29
BRu(bpym)OsB ⁴⁺				1.18	Os ^{II} → Os ^{III}	28, 29

For the mononuclear complex [Re^ICl(CO)₃(dpq)] the first reduction associated with the ligand dpq occurs at -0.83 V (vs. s.c.e.), in the same region as measured for [Os(bipy)₂(dpq)]²⁺ during the course of this work and for [Ru(bipy)₂(dpq)]²⁺ reported earlier.¹⁶ Upon binucleation, the first reduction wave anodically shifts by ca. 400 mV in Re-Re, Re-Ru, and Re-Os complexes. The magnitude of the shifts are similar to those observed for homobinuclear complexes of Ru and Os.

Except for the heterobinuclear complexes cited below, the first oxidation waves of the mono- and bi-nuclear rhenium(I) complexes invariably are irreversible, showing a partial reduction wave during the reverse scan at high scan rates ($\geq 200 \text{ mV s}^{-1}$). Hence, the oxidation potentials listed in Table 3 are

peak potentials. Our observations are consistent with the known irreversibility of the oxidation Re^I to Re^{II} carbonyl polypyridyl complexes.^{28-31,35,36} The electrochemical oxidation behaviour of the mixed-metal Re-Ru complexes with dpp and dpq as bridging ligands is very similar to that described recently by Rillema *et al.*³⁰ for the analogous bpym complex. It appears that the Re^I-Re^{II} and Ru^{II}-Ru^{III} oxidations are very nearly isoenergetic as indicated by two nearly superimposed waves exhibiting partial reversibility at high scan rates. It is likely that the more positive wave corresponds to irreversible Re^I-Re^{II} oxidation and the earlier shoulder to the Ru^{II}-Ru^{III} couple.

In the heterobinuclear complex involving osmium, [ARe^I-

Table 4. Data on the luminescence of the homo- and hetero-binuclear ligand-bridged polypyridyl complexes of Ru, Os, and Re

Complex ^c	a		b		Ref. ^d
	$\lambda_{\text{max.}}/\text{nm}$	τ/ns	$\lambda_{\text{max.}}/\text{nm}$	$\tau/\mu\text{s}$	
Monomeric complexes					
[ReCl(CO) ₃ (bipy)]	614 (625)	50	532	2.74	35
[ReCl(CO) ₃ (bpym)]			540	0.22	29
[ReCl(CO) ₃ (dpp)]	650 (700)	≤20	590	0.76	t.w.
Binuclear complexes					
ARe(dpp)ReA	790	≤20	690	0.28	t.w.
ARe(dpp)RuB ²⁺	770		697, 765	1.96	t.w.
BRu(dpp)RuB ⁴⁺	727 (770)	140	702, 770	2.38	15

^a Emission at room temperature in CH₂Cl₂. Corrected values in parentheses. ^b Emission at 77 K in EtOH. ^c A and B are as denoted in Table 2. ^d t.w. = This work.

(dpp)Os^{II}B]²⁺, the first oxidation is reversible and occurs at +1.10 ± 0.07 V, nearly 200 mV more positive to that observed in related osmium complexes: ¹⁴ [Os(bipy)₂(dpp)]²⁺. BOs(dpp)-RuB, and BOs(dpp)OsB. It should however be mentioned that the peak separation for binuclear complexes is much larger (≈150 mV). Hence the first oxidation is unambiguously assigned as Os^{II}→Os^{III}. For comparison, we have included in Table 3 corresponding values for the oxidation and reduction reported earlier for mono- and bi-nuclear carbonyl bipyrimidine complexes of Re^I.^{28,31} For bipyrimidine as the bridging ligand, the anodic shift in the first reduction wave upon binucleation is substantial (≥500 mV).

Luminescence.—The luminescence properties of the mono- and bi-nuclear complexes were investigated in methylene chloride solutions at room temperature and in EtOH–MeOH (4:1) glass at 77 K and the results are summarized in Table 4. Carbonyl polypyridine complexes of Re^I are known to exhibit weak emissions corresponding to L→M c.t. transitions. Examination of the data in Table 4 reveals several aspects of the luminescence of these complexes. The emission from 'dpp' complexes is red-shifted and comparatively short-lived as compared to analogous 'bipy' complexes.

The weak yet clearly detectable emission from the Re(dpp)Re complex represents the first example of an emissive strongly coupled binuclear rhenium complex. The emissive binuclear complex [{ReCl(CO)₃]₂(tmqpy)] of Juris *et al.*²⁹ referred to in the introductory paragraphs represents a weakly interactive case. The similarity in the emission maximum of the heterobinuclear Re(dpp)Ru complex with that of the homobinuclear complex Re(dpp)Re renders assignment of the former emission ambiguous. The longer lifetime (1.96 μs) of the heterobinuclear complex [comparable to that of the homobinuclear Ru(dpp)Ru complex] clearly suggests the emission is ruthenium based.

Within the detection range (up to 850 nm) and sensitivity limits ($\phi \geq 10^{-4}$) of our spectrofluorimeter, we couldn't detect any authentic emission from any of the mono- and bi-nuclear rhenium complexes with dpq as the bridging ligand. It is known that even for ruthenium complexes with dpq the luminescence yields are extremely low.¹⁶

Conclusions

In continuation of our studies on the characterization and photophysics of ligand-bridged polypyridyl complexes^{14,15} in this work we have characterized some homo- and heterobinuclear complexes involving Re^I and dpp. The shifts in the absorption spectral and redox properties of the mononuclear complex upon binucleation are very similar to that observed earlier with analogous complexes of Ru and Os. For the heterobinuclear Re(dpp)Ru complex, while the irreversibility of the rhenium-based oxidations renders assignment of the lowest-energy excited state ambiguous, luminescence data clearly indicate emission occurring from a ruthenium-based c.t. excited state. It has been shown earlier that, for polypyridyl complexes containing 'Cl' or 'bpym' as inner-sphere ligands, radiative decay is an inefficient pathway and this may account for the lack of any luminescence from [{ReCl(CO)₃]₂(bpym)]. Recent reports of long-lived and highly luminescent emission from complexes of the type [Re(CO)₄L] strongly suggest the corresponding binuclear complex [{Re(CO)₄]₂(dpp)] to be a promising candidate in the search for luminescent binuclear rhenium carbonyl polypyridyl complexes. Studies towards examination of such conjunctures are currently underway.

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