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Excited-state acid–base chemistry of coordination complexes

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Dedicated to Arthur W. Adamson, an excellent scientist, mentor and colleague, on the occasion of his 80th birthday

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Abstract

Photoactivation of $Ru(bpy)_2dpp^{2+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine) in the presence of MCl_6^{n-} (M = Pt(IV), Rh(III), Pd(IV)) leads to quantitative formation of the corresponding bimetallic

$$^*Ru(bpy)_2(dpp)^{2+} + MCl_6^{n-} \rightarrow [Ru(bpy)_2(dpp)MCl_4]^{4-n} + 2Cl^-$$

Formation of the bimetallic does not occur by either electron- or energy-transfer processes. Instead, population of the MLCT state in $Ru(bpy)_2(dpp)^{2+}$, localized on the dpp ligand, increases the electron density on peripheral nitrogens as evidenced by an order of magnitude greater than six, increase in their Brønsted basicity relative to that of the ground state. The increased electron density promotes an excited-state coordination chemistry, where changes in coordination, rather than energy or electron transfer, leads to emission quenching and subsequent formation of the bimetallic. The enhanced basicity exists only in the excited state, and coordination of the second peripheral nitrogen, i.e. the chelate effect, competitive with relaxation of the excited state achieves the observed, thermodynamically stable product. This

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article summarizes the excited-state proton-transfer chemistry of Ru(II) diimine complexes, and discusses the application of this chemistry to excited-state coordination chemistry and the formation of bimetallic complexes.

Keywords: Excited-state proton transfer; Ru(II) Diimines; Excited-state coordination

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Experiments in this laboratory reveal an unusual photochemistry where excitation of complexes capable of acting as a ligand in the presence of other transition metal ions leads to the formation of a bimetallic complex [1,2]. For example, excitation of bis(2,2′-bipyridine)(2,3-bis(2-pyridyl)pyrazine)ruthenium(II), $(bpy)_2Ru(dpp)^{2+}$, in the presence of MCl_6^{n-} (M = Pt(IV), Rh(III) and Pd(IV) leads to the formation of the corresponding bimetallic

$$^*(bpy)_2Ru(dpp)^{2+} + MCl_6^{n-} \rightarrow [(bpy)_2Ru(dpp)MCl_4]^{4-n} + 2Cl^- \quad (1)$$

Electron- and energy-transfer quenching of Ru(II) diimines are well established, but the absence of an equivalent reaction with metals known to quench by these mechanisms, the specificity of bimetallic formation and the energetics of the reactants lead us to propose a different reaction mechanism. The MLCT state of $(bpy)_2Ru(dpp)^{2+}$ is localized on the dpp ligand, and quenching of this state by $[H^+]$ indicates that excitation increases the basicity of the peripheral nitrogen atoms by more than six orders of magnitude [3,4]. We propose that the increased electron density corresponding to this immense increase in basicity translates into an excited state coordination chemistry, where changes in coordination, rather than energy or electron transfer, leads to emission quenching and subsequent formation of the bimetallic. Here, we review the proton transfer chemistry of the MLCT states of Ru(II) diimine complexes, and discuss the application of this excited-state acid–base chemistry to the formation of polymetallic complexes

The realization of an excited-state acid–base chemistry stems from the Weber's observations that the blue–violet emission from 1-naphthylamine-4-sulphonate in neutral solution changes to green with increasing pH [5]. Subsequent quantitative experiments revealed surprisingly large changes in Brønsted acidity or basicity depending on the specifics of the molecule being excited, and the specific state produced [6,7]. Triplet states exhibit relatively moderate changes in pK_a relative to the ground state, whereas those of the singlet states differ by five to more than ten orders of magnitude [8–11]. Studies during the past 15 years have detailed the rates and theory of proton transfer [12–18]; the role of the solvent in the transfer process [19–24], and the sites of excited state protonation [25,26]. Less attention has been paid to the chemical consequence of the changes in excited state acidity and basicity. Reflecting the short excited-state lifetime and large ΔpK_a, excited-state proton-transfer catalysis is most pronounced in intramolecular reactions occurring via the excited singlet state [27]. Photoinitiated nitrosation of naphthols [28], the photoinduced cyclization of allyl–naphthols [29–31], the photohydration of aromatic alkenes [32] and the photocyclization of phenols [9] are currently thought to occur via an excited state proton transfer, although in the latter case, i.e. the photocyclization of phenols, an alternative electron transfer mechanism has been suggested [33].

Fewer examples of excited-state proton transfer exist amongst transition metal complexes [34] with no information available beyond proton transfer rates derived from the quenching data on the chemical consequences of these photoinduced changes in acidity and basicity. Available data are limited to Ru(II) diimines. Nevertheless, it is clear that optical excitation produces equally striking changes in Brønsted acid–base properties. Population of the emissive MLCT state of these complexes can, depending on the specifics of the charge transfer, increase or decrease basicity from two to close to nine orders of magnitude. Optical excitation of *cis*-$Ru(bpy)_2(CN)_2$, for example, produces an emissive MLCT state where charge is transferred from Ru(II) to the bipyridine ligands [35]. In a formal sense, the MLCT state corresponds to a Ru(III) coordinated to a bpy^- radical anion. The increased positive charge at the metal center inductively reduces the charge density at the cyano group, and the redistributed charge reduces the basicity at the nitrogen atom of the coordinated cyanide by greater than five orders of magnitude relative to that in the ground state. Hence, the excited MLCT state is a substantially weaker base than the ground state [35]. Similarly, the MLCT states of $(bpy)_2Ru(phen(OH)_2)^{2+}$, $(4,4'\text{-}Me_2bpy)_2Ru(phen(OH)_2)^{2+}$, $((phen)_2Ru(phen(OH)_2)^{2+}$ and $(3,4,7,8\text{-}Me_4phen)_2Ru(phen(OH)_2)^{2+}$, where $phen(OH)_2$ denotes 4,7-dihydroxy-1,10-phenanthroline ($phen(OH)_2$) are weaker bases, or stronger acids than the corresponding ground states of the complexes [36]. The ground state pK_a values of $(bpy)_2Ru(phen(OH)_2)^{2+}$, $(4,4'\text{-}Me_2bpy)_2Ru(phen(OH)_2)^{2+}$, $(phen)_2Ru(phen(OH)_2)^{2+}$ and $(3,4,7,8\text{-}Me_4bpy)_2Ru(phen(OH)_2)^{2+}$ are 10.1, 10.0, 10.0 and 9.8, respectively, while the excited state pK_a values are 5.1, 5.4, 4.7 and 4.2, respectively [36]. Proton NMR reveals significant changes in electronic structure on going from the protonated to the unprotonated forms of coordinated $phen(OH)_2$. The spectra suggest that the unprotonated form of the hydroxylated ligand stabilizes the hole on the ruthenium ion, generated by the charge transfer transition, via π donation. This decreases the electron density in the ligand thereby increasing the acidity of the peripheral hydroxyl groups [34]. As with *cis*-$Ru(bpy)_2(CN)_2$, the increased acidity on excitation is thought to be a consequence of charge transfer to the ligands not involved in the proton transfer per se. Instead, inductive coupling reduces the electron density in the $phen(OH)_2$ ligand thereby facilitating proton loss. In view of the role of the inductively coupled ligand, it is interesting to note the effect of the methyl groups, which are weak electron donors. In the ground state, the methyl substituents on the bpy and phen ligands have no effect beyond experimental error on the acidity of the coordinated $phen(OH)_2$. In the MLCT state, however, their effect is more pronounced. Relative to bpy, the two methyl groups of $4,4'\text{-}Me_2bpy$ increase the pK_a^* by 0.3 ± 0.2, while the four methyl groups in $(3,4,7,8\text{-}Me_4phen)_2Ru(phen(OH)_2)^{2+}$ increase the pK_a^* by 0.8 ± 0.2 [36].

The more common situation, and the focus of this review, is the increases in apparent Brønsted basicity that occurs on excitation of Ru(II) complexes containing ligands with either carboxylates, or one or more pyridine-like nitrogens on the outer periphery of a coordinated diimine ligand. The general view of the MLCT state(s) of these complexes is Ru in the +3 oxidation state and an electron in one of the polypyridyl ligands [37]. In mixed ligand complexes, the electron transferred in the excited state is generally localized on the most easily reduced ligand [37]. With attached carboxylates, such as 4,4′-dicarboxy-2,2′-bipyridine, or 5,5′-dicarboxy-2,2′-bipyridine, the electron density transferred on excitation localizes in the dicarboxy ligands thereby increasing their basicity [3,38–40]. For example, the first pK_a of bis(2,2′-bipyridine)(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II), $Ru(bpy)_2$-(4,4′-dcbpy) increases from 2.85 in the ground state to 4.25 in the MLCT state [36]. Similar changes, $\Delta pK_a = 1.9 \pm 0.5$, occur for the first protonations of Ru(bpy)(4,4′-dcbpy)$_2$ and Ru(4,4′-dcbpy)$_3$, while that for Ru(5,5′-dcbpy)$_3$ is 1.0 [3,38]. With each complex, excitation increases the basicity for the first protonation, but does not change the basicity for the second protonation. Protonation shifts the emission to the red and reduces its intensity. The emission intensity from the protonated form of $Ru(bpy)_2$(4,4′-dcbpy) decreases to ca. 1% of that from the deprotonated complex. What is surprising is the absence of an equivalent change in the lifetimes of the protonated and deprotonated complexes. The lifetime of the deprotonated form of $Ru(bpy)_2$(4,4′-dcbpy) at pH 7.0, 395 ns, is very similar to that of the full protonated species at pH 0, 320 ns [3,39]. Although the exchange of protons with the solvent medium might be expected to affect the coupling with the solvent medium, the similarity of the lifetimes of the dicarboxlated complexes implies that the large change in the emissivity of the protonated complex is not due to an increase in the nonradiative rate. Rather, in these complexes, it is due principally to a change in the radiative rate constant, k_r. Correcting the ratio of emission quantum yields of the protonated and deprotonated complexes, 0.01, for the difference in the lifetimes shows that protonation reduces the radiative rate constant for the protonated complex by a factor of ca. 100 relative to that in the deprotonated complex. It is worthwhile to note, in this regard, that the radiative rate is a function of the molecular and electronic structure of the emitter, and not dependent on the coupling to the solvent medium. At least in these complexes, the principal effect of protonation and deprotonation is not a change in the coupling with the solvent medium.

Like the dicarboxylated derivatives, excitation of Ru(II) complexes containing ligands with one or more pyridine-like nitrogens on the outer periphery of the diimine ligand creates a Ru(III)–ligand radical anion MLCT state [37]. Particularly in mixed ligand complexes, the charge generally localizes in the ligand containing the peripheral nitrogens, and consistent with the electronegativity of the peripheral nitrogens, resonance Raman spectra of $Ru(bpy)_2(dpp)^{2+}$ and $Ru(bpy)_2(ppz)^{2+}$ (ppz denotes [4,7]phenanthrolino[5,6]bipyrazine) indicate that the majority of the electron density resides on or near the peripheral nitrogens [4]. This transfer of charge in the excited state leads to immense increases in the Brønsted basicity of the peripheral nitrogens [3,4,37,41,42]. The acid dissociation constants for the ground state, pK_a, excited state, pK_a^*, and the change in pK_a, ΔpK_a, for complexes of this type, along with the lifetime of the deprotonated complex, τ, and the bimolecular rate of proton addition, k_b (H^+) are listed in Table 1. The values are listed as equilibrium constants, i.e. as pK_a values, but it is important to point out that, at this time, it is not clear whether the reported values are the actual equilibrium values. The uncertainity arises from the question of whether the excited states of these complexes actually have sufficient time to equilibrate. Corrections can be made for differences in the lifetimes of the protonated and deprotonated forms of species exhibiting excited-state acid–base equilibria, but with most of these complexes, the protonated forms of the complexes do not emit.

Two exceptions are tris(tetraazaphenanthracene)ruthenium(II), $Ru(TAP)_3^{2+}$, and tris(bipyrazine)ruthenium(II), $Ru(bpz)_3^{2+}$. $Ru(TAP)_3^{2+}$ and $Ru(bpz)_3^{2+}$ exhibit emission maxima at 595 nm, while the monoprotonated forms, $Ru(TAP)_2(TAPH)^{3+}$ and $Ru(bpz)_2(bpzH)^{3+}$ emit with maxima at 800 and 717 nm, respectively [41,42]. In both cases, protonation reduces emission intensity and lifetime. The emission intensity from $Ru(bpz)_2(bpzH)^{3+}$ is $\leq 0.5\%$ of that from the unprotonated complex [41], while the emission lifetime of $Ru(TAP)_2(TAPH)^{3+}$,

Table 1

Ground and excited state pK_a values, lifetimes, and bimolecular rate constants for H^+ addition

Complex*		pK_a	pK_a^*	ΔpK_a	τ (ns)	k_b $(H^+) \times 10^{-10}$ $(M^{-1}\ s^{-1})$	Reference
1	$Ru(bpz)_3^{2+}$	−2.2	2.0	4.2	900	–	[41]
		–	–	3.3	940	0.7	[3]
2	$Ru(Me_2bpy)_2(dpp)^{2+}$	−3.7	2.8	6.5	64	–	[3]
3	$Ru(bpy)_2(dpp)^{2+}$	−3.8	2.8	6.6	127	0.5	[3]
4	$Ru(phen)_2(dpp)^{2+}$	−4.0	3.0	7.0	202	–	[3]
5	$Ru(5\text{-}Clphen)_2(dpp)^{2+}$	–	3.2	–	260	–	[3]
6	$Ru(dpp)_3^{2+}$	−4.8	3.5	8.3	270	–	[3]
7	$Ru(bpy)_2(bpym)^{2+}$	−2.9	2.0	4.9	13	–	[3]
		–	1.9	–	14	–	[37]
8	$Ru(bpm)_3^{2+}$	–	2.4	–	77	–	[37]
		−1.0	2.2	3.2	83	–	[3]
9	$Ru(TAP)_3^{2+}$	−3.0	3.5	6.5	230	1.0	[42]
10	$Ru(TAP)_2(bpy)^{2+}$	−2.6	4.0	6.6	620	1.0	[42]
11	$Ru(TAP)(bpy)_2^{2+}$	−2.0	3.1	5.1	130	1.0	[42]
12	$Ru(bpz)_2(bpm)^{2+}$	–	3.4	–	710	0.7	[37]
13	$Ru(bpm)_2(bpz)^{2+}$	–	3.5	–	520	0.7	[37]
14	$Ru(bpz)_2(bpy)^{2+}$	–	3.4	–	400	–	[37]
15	$Ru(bpy)_2(bpz)^{2+}$	–	2.8	–	92	–	[37]
16	$Ru(bpy)(bpm)(bpz)^{2+}$	–	3.1	–	220	–	[37]
17	$Ru(bpm)_2(bpy)^{2+}$	–	2.2	–	44	–	[37]

* The number of each complex corresponds to the numbers in Fig. 1. Ligand abbreviations: Bpm or Bpym, 2,2′-bipyrimidine; Dpp, 2,3-bis(2-pyridyl)pyrazine; 4,4′-dcbpy, 4,4′-dicarboxy-2,2′-bipyridine; 5,5′-dcbpy, 5,5′-dicarboxy-2,2′-bipyridine; Bpz, 2,2′bipyrazine; TAP, 1,4,5.8-tetraazaphenanthrene; Bpy, 2,2′-bipyridine; Phen, 1,10-phenanthroline; 5-Cl-phen, 5-chloro-1,10-phenanthroline; Me_2bpy, 4,4′-dimethyl-2,2′-bipyridine.

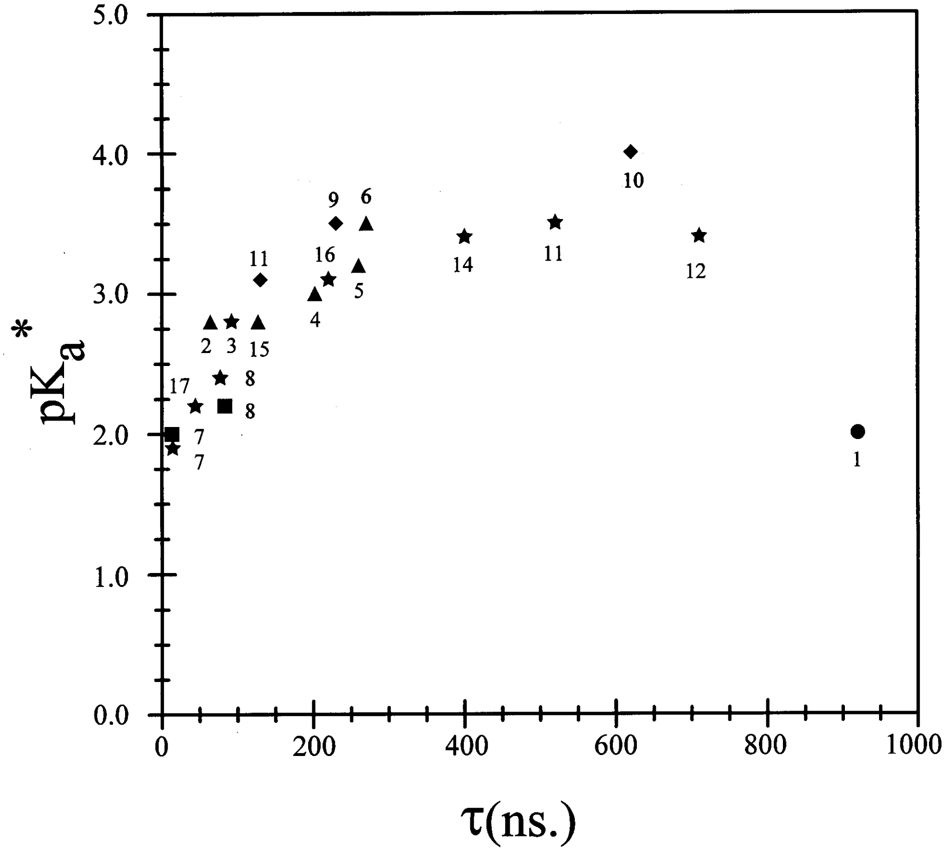

Fig. 1. The pK_a^* for the different complexes vs. the lifetime of the MLCT state of the unprotonated complex. The numbers adjacent to the individual points refer to the number of the complex in Table 1.

< 30 ns, is considerably less than that of Ru(TAP)$_3^{2+}$, 230 ns [42]. Unlike the dicarboxylate substituted complexes described above [3,38–40], where protonation principally reduces the radiative rate constant, protonation of these diimines affects both the radiative and nonradiative rates of decay.

As noted, it is not clear whether the reported values of pK_a^* (Table 1) are the actual values of the equilibrium constants. Equilibrium is used in the sense that the value describes a ratio of the protonated and deprotonated forms of a complex that is not changing with time beyond that attributable to the excited–state lifetime of the protonated and deprotonated forms. If the excited state does not have sufficient time to achieve a time invariant ratio, then the measured pK_a^* is expected to depend on the excited state lifetime. A plot of the acid dissociation constants reported for the monoprotonated, excited complexes, pK_a^*, versus the lifetime of the deprotonated complex (Fig. 1) reveals a clear dependence on excited state lifetime. With the exception of Ru(bpz)$_3^{2+}$, the values of pK_a^* for the different complexes are closely grouped with complexes possessing similar MLCT state lifetimes exhibiting similar $\mathrm{p}K_a^*$ values. For example, the $\mathrm{p}K_a^*$ values of $^*\mathrm{Ru(dpp)_3^{2+}}$ and $^*\mathrm{Ru(TAP)_3^{2+}}$, which have lifetimes of 270 and 230 ns, respectively, are identical, 3.5 [3,42]. This contrasts sharply with the ground state behavior, where the $\mathrm{p}K_a$ of $\mathrm{Ru(dpp)_3^{2+}}$, -4.8, differs by 1.8 from that of $\mathrm{Ru(TAP)_3^{2+}}$, -3.0. The similarity of the $\mathrm{p}K_a^*$ values of structurally different complexes and the dependence of $\mathrm{p}K_a^*$ on the lifetime of the deprotonated complex leads us to suspect that complexes with MLCT state lifetimes of ≤ 200 ns do not achieve a time-invariant ratio of the protonated and unprotonated forms of the complexes. The $\mathrm{p}K_a^*$ values of complexes with lifetimes of ≥ 300 ns exhibit a much smaller dependence on excited state lifetime suggesting that these complexes do achieve a time invariant ratio, or come very close it. The ability to achieve a time independent ratio, or what we will refer to as equilibrium, is not due to differences in the rates of proton transfer. The bimolecular rates of proton transfer, designated k_b (H^+) in Table 1 and calculated from the Stern–Volmer constants for H^+ quenching and the lifetime of the deprotonated complex, are essentially diffusion limited regardless of the excited-state lifetime. Complexes with short excited-state lifetimes, such as $\mathrm{Ru(bpy)_2(dpp)^{2+}}$, 127 ± 30 ns, and $\mathrm{Ru(bpy)_2(TAP)^{2+}}$, 130 ns, exhibit proton transfer rate constants, 5×10^9 $\mathrm{M^{-1}\ s^{-1}}$ and 1×10^{10} $\mathrm{M^{-1}\ s^{-1}}$, respectively, within experimental error of complexes possessing much longer excited state lifetimes. The excited state lifetime of $\mathrm{Ru(bpz)_3^{2+}}$ is 920 ± 20 ns [41], yet the bimolecular rate constant of proton transfer, 7×10^9 $\mathrm{M^{-1}\ s^{-1}}$, is most likely within experimental error of those of $\mathrm{Ru(bpy)_2(dpp)^{2+}}$ and $\mathrm{Ru(bpy)_2(TAP)^{2+}}$. Although the rate constants are diffusion limited, the product k_b $[\mathrm{H}^+]$ is the relevant parameter with respect to intercepting the excited state, and it is not clear to us that this product is sufficient to achieve equilibrium in each experiment. We can only speculate at this point, but since the rate constants for proton transfer are essentially diffusion limited, we wonder if the dependence of $\mathrm{p}K_a^*$ on the excited state lifetime shown in Fig. 1 reflects only the addition or loss of the proton per se. It might reflect entropic factors arising from the reorganization of the surrounding solvent necessary to accommodate the addition of, or loss of, the proton. In other words, proton addition or loss from these molecules occurs at a diffusion-limited rate. Whether the system achieves an invariant ratio corresponding to an energy minimum, however, is not determined solely by the gain or loss of the proton, but by the change in the surrounding solvent that must occur to accommodate proton addition or loss. In the ionization of organic acids, for example, the enthalpic factors associated with specific inductive, resonance or structural effects do not control the relative stability of the Brønsted acid and its conjugate base [43]. Rather, the principal determinant of the free energy is the change in entropy associated with an extensive reordering of the solvent that occurs about the charged ionization products [43]. With complexes such as these, which already possess a $+2$ charge, it is reasonable to question whether the addition or loss of a proton will produce solvent reorganization sufficient to account for the observed change in $\mathrm{p}K_a$. In spite of the charge, however, the outer volumes of these diimine complexes are relatively hydrophobic. Particularly in mixed ligand complexes where the hydrophobicity of the ligands differ, an MLCT state localized on a specific ligand which is subsequently protonated could result in large entropy terms due to solvent reorganization. In this regard, note that of the 18 complexes listed in Table 1, the two that are luminescent in the protonated form, $\mathrm{Ru(bpz)_3^{2+}}$ and $\mathrm{Ru(TAP)_3^{2+}}$, possess three equivalent ligands. Are these complexes, because each ligand possesses peripheral acid–base sites (pyridine-like nitrogens) more extensively hydrogen bonded in the ground state than a complex with a coordination shell composed of bipridines or phenanthrolines and one or two ligands possessing peripheral acid–base sites? In the tris complexes, is there less solvent reorganization in the excited state than complexes containing different ligands of differing hydrophobicity? This is clearly speculation on our part since there are also two other complexes, $\mathrm{Ru(dpp)_3^{2+}}$ and $\mathrm{Ru(bpym)_3^{2+}}$ [$\mathrm{Ru(bpm)_3^{2+}}$]($\mathrm{Ru(bpm)_3^{2+}}$ and $\mathrm{Ru(bpym)_3^{2+}}$ are the same complexes with bpm or bpym indicating 2,2′-bipyrimidine [3,37]) that also possess three equivalent ligands, yet there are no reports in the current literature that the protonated forms of these complexes are emissive. Solvent reorganization might also be expected to affect the lifetime of the excited states, yet $\mathrm{Ru(dpp)_3^{2+}}$, exhibits an emission lifetime, 270 ns, very similar to that of $\mathrm{Ru(TAP)_3^{2+}}$, 230 ns. Further measurements of emission lifetime and emission quantum yield for both the protonated and unprotonated forms of the complexes in solvent of differening polarity and hydrogen bonding facility are needed to determine whether solvent reorganization contributes to the observed ΔpK_a.

Many factors affect excited-state lifetime and Brønsted acidity and basicity, but the close similarity of the pK_a^* values and the sharp dependence of pK_a^* on lifetime (Fig. 1) lead us to suspect that the reported values are kinetically limited in the sense that the system is not achieving the time-invariant ratio corresponding to the actual pK_a^*. Specifically, the values of pK_a^* reported for complexes with excited state lifetimes of ≤ 200 ns appear to be kinetically limited, in which case, the reported pK_a^* are most likely low estimates of the actual value. The values of pK_a^* for complexes with lifetimes of ≥ 200 ns change much less with lifetime suggesting that in these cases, the complexes manage to achieve equilibrium, or come very close to it. Hence, these values are considered equilibrium, or close to the equilibrium values. Perhaps reflecting the fact that the shorter excited-state lifetime species do not achieve full equilibrium, the ground states of complexes 1–11 in Table 1 exhibit a wider variation in pK_a, 2.8, than do the corresponding excited states, 2.0. This contrasts with the behavior of the complexes containing the $\mathrm{phen(OH)_2}$ ligand, where excitation reduces basicity leading to proton loss (the results are therefore independent of the $[\mathrm{H}^+]$) and magnifies the effect of the methyl substituents relative to that in the ground state. Alternatively, the reduced variation in pK_a^* might be attributed to a ‘leveling effect’ where the excited state ‘focuses’ electron density within a given ligand. The highest electron density within a given ligand occurs in the radical anion created by one electron reduction of the complex [37]. Formally a ligand radical anion coordinated to Ru(II), the one–electron reduction product is expected to have a higher electron density within the most easily reduced ligand than the MLCT state, which is formally Ru(III) coordinated to the ligand radical anion. This expectation is borne out by the relationship found for the bpy, bpz and bpm complexes (complexes 11–18 in Table 1) where the pK_a for the protonated form of the one-electron reduced complex is related to the pK_a^* of the excited state by the relation $pK_a - pK_a^* = 4.8$ [37]. This relationship implies that the variation in pK_a^* found for complexes 11 through 18 in the MLCT state also occurs with the one electron reduction product which, judging from the ca. 10^5 increase in pK_a, has a higher electron density in the ligand. At least in these complexes, increasing the charge density in the ligand does not 'level out' the differences in basicity between the complexes. Regardless of whether the excited state achieves equilibrium, clearly optical excitation produces startling changes in apparent basicity as evidenced by enhanced ability of the excited complexes to bind a proton. The changes in basicity range from about three orders of magnitude for $Ru(bpz)_3^{2+}$ and $Ru(bpm)_3^{2+}$, to more than eight orders of magnitude for $Ru(dpp)_3^{2+}$. The largest changes in basicity are found with the $Ru(bpy)_{3-n}(dpp)_n^{2+}$ ($n = 1, 2, 3$) complexes where the excited state is localized on the dpp [3,4]. Developing specific structure–function relationships is tenuous at this point, but the large change found with $Ru(dpp)_3^{2+}$, $\Delta pK_a = 8.3$, and the relatively large changes found with $Ru(bpy)_2(dpp)^{2+}$, $\Delta pK_a = 6.6$, suggest that delocalization of the excited state amongst equivalent ligands, as opposed to localizing the charge in a specific ligand, does not significantly reduce the basicity in the excited state. Alternatively, charge localization within a specific ligand is consistent with the current data which show rapid localization of the charge in a specific ligand in $Ru(bpy)_3^{2+}$. In spite of the uncertainties in the specific values of pK_a^* and ΔpK_a, there is little question that excitation dramatically increases the Brønsted basicity, and as noted by one reviewer, "pK_a^* is certainly higher than that in the ground state" [3].

Our interest focuses on the changes in electron density corresponding to the increased Brønsted basicity. Specifically, does the large change in Brønsted basicity translate into an excited-state Lewis acid–base chemistry, where changes in coordination, rather than electron or energy transfer, lead to a net chemical change. We contend they do, and our contention arises from the observation that excitation of $(bpy)_2Ru(dpp)^{2+}$, in the presence of MCl_6^{n-} (M = Pt(IV), Rh(III) and Pd(IV) leads to the formation of the corresponding bimetallics, $[(bpy)_2Ru(dpp)MCl_4]^{4-n}$, reaction 1 [1,2]. Electronic spectra recorded during photolysis exhibit isosbestic points indicating quantitative conversions through, in the case of $[(bpy)_2Ru(dpp)PtCl_4]^{2+}$ formation, as much as 70% conversion. Emission intensity and lifetime quenching, under conditions of minimal ion pairing (3 M NaCl), establish a diffusional encounter characterized by a Stern–Volmer constant of 407 ± 41 M^{-1}. The latter value agrees with that obtained from the photochemical data, and the reduction in the yield of the bimetallic in presence of a competitive quencher, Fe^{3+}, establish bimetallic formation via a collision between $^*(bpy)_2Ru(dpp)^{2+}$ and $PtCl_6^{2-}$ [1,2].

The energetics of the reactants suggests that bimetallic formation does not occur via photoinduced electron, or energy transfer. The dpp localized MLCT state lies 1.48 eV above the ground state [1,2,44,45], while the $^1T_1$ state of $PtCl_6^{2-}$ lies 3.5 eV above the ground state [46]. The spin-forbidden $^3T_2$ state lies at 2.8 eV, while the $^3T_1$ is calculated to lie 2 eV above the ground state [1,2,47]. The energy of the quintet state, $^5T_2$, is calculated to be very close of that of the $^3T_1$ state, i.e. 2 eV [1,2,47]. Clearly uncertainies exist in the estimation of these energies, but the triplet and quintet states are not expected to be ≤ 1.48 eV, making energy transfer endergonic. Similarly, photoinduced electron transfer seems equally unlikely. The oxidation potential of $^*(bpy)_2Ru(dpp)^{2+}$ is calculated to be 0.25 eV (vs. NHE) [1,2,44], while the reduction potential of $^*(bpy)_2Ru(dpp)^{2+}$ is estimated to be about 1.0 eV [48]. We can not rule out electron transfer on the basis of thermodynamics since the one electron oxidation and reduction potentials of $PtCl_6^{2-}$, $PdCl_6^{2-}$ and $RhCl_6^{3-}$ are not known, although in the case of Pt(IV) and Pd(IV) oxidative or reductive quenching would lead to the unusual oxidation states of $+3$ or $+5$.

Experiments with metals known to quench by either electron transfer, or energy transfer also suggest a different mechanism. Electron transfer quenching of $Ru(bpy)_3^{2+}$ by Fe^{3+} is well established, and oxidative quenching of $Ru(bpy)_2(dpp)^{2+}$ is exergonic by 1.0 V. Furthermore, both Fe^{3+} and Fe^{2+} form stable complexes with diimine ligands [49]. The equilibrium constant for the coordination of a phenanthroline ligand onto Fe^{2+}, for example, is 7×10^5. Hence, if electron transfer quenching is involved, oxidative quenching by Fe^{3+} is expected to lead to bimetallic formation. The standard potential for the $Co(H_2O)_6^{3+}/Co(H_2O)_6^{2+}$ couple, 1.84 V in 4 M HNO_3 [50], suggests energy transfer quenching, and Co(II) is substitution labile. $Cr(H_2O)_6^{3+}$ quenches by energy transfer [51], forms stable diimine complexes, and the trivalent metal ion is substitution inert [52]. Consequently, if energy transfer were to occur and form a coordinatively unsaturated species, coordination to the peripheral nitrogens of dpp, is expected to produce a substitution–inert product. Although each metal ion quenches $^*Ru(bpy)_2(dpp)^{2+}$, the limiting yield of bimetallic formation is negligible, $\Phi_{bi} \leq 10^{-3}$. In fact, a survey of metal complexes shows that in the cases where photoinduced electron transfer is thermodynamically favored, photoinduced formation of the bimetallic is not observed. For example, oxidative quenching of $^*Ru(bpy)_2(dpp)^{2+}$ by $OsCl_6^{2-}$ and $IrCl_6^{2-}$ are exergonic by 1.10 and 1.12 V [50], respectively, but there is no indication of bimetallic formation in the corresponding photochemical experiments.

The specificity of the reactions also points to a different reaction mechanism. Central to an energy or electron transfer process is the formation of a more labile intermediate. In aqueous solution, formation of a labile oxidation state, or a coordinatively unsaturated intermediate would result in water coordination, ligand scrambling and a distribution of products containing differing amounts of coordinated water. Yet with $PtCl_6^{2-}$, the conversion to the bimetallic is quantitative, as evidenced by two isosbestic points maintained through as much as 70% conversion, at which point photolysis of the bimetallic occurs. Previous studies of $PtCl_6^{2-}$ suggest that exchange with radiolabeled chloride is catalyzed by a Pt(III) complex present in trace amounts [53]. Attributing bimetallic formation to some undefined mechanism involving a catalytic Pt(III) impurity, however, is not consistent with the effect of added $PtCl_4^{2-}$. The Pt(III) catalyst can be generated in situ by a number of different routes, one being the reaction $PtCl_6^{2-} + PtCl_4^{2-} \rightarrow 2PtCl_5^{2-}$ [53]. However, the addition of $PtCl_4^{2-}$ in amounts ranging from 10^{-8} to 5.6×10^{-5} M to solutions 5.0×10^{-5} M in $(bpy)_2Ru(dpp)^{2+}$ and 10^{-3} M in $PtCl_6^{2-}$ has no effect beyond experimental error on the yield of $[(bpy)_2Ru(dpp)PtCl_4]^{2+}$ (Fig. 2). Furthermore, similar quantitative conversions to the bimetallic occur with $PdCl_6^{2-}$ and $RhCl_6^{3-}$, and to our knowledge, there is no evidence that the substitution chemistry of the Rh(III) complex, in particular, is promoted by a catalytic impurity. The extent of quantitative conversion to the bimetallic with these hexachlorides is limited by a competitive aquation, yet spectra recorded during photolyses indicate quantitative conversion to the bimetallic through at least 22 and 37% conversion, respectively.

The absence of bimetallic formation with metals known to quench by electron transfer or energy transfer, the lack of enhancement of the yield of the bimetallic in the presence of $PtCl_4^{2-}$, the specificity of the reaction, and the energetics of the reactants lead us to suggest a different quenching mechanism for the formation of

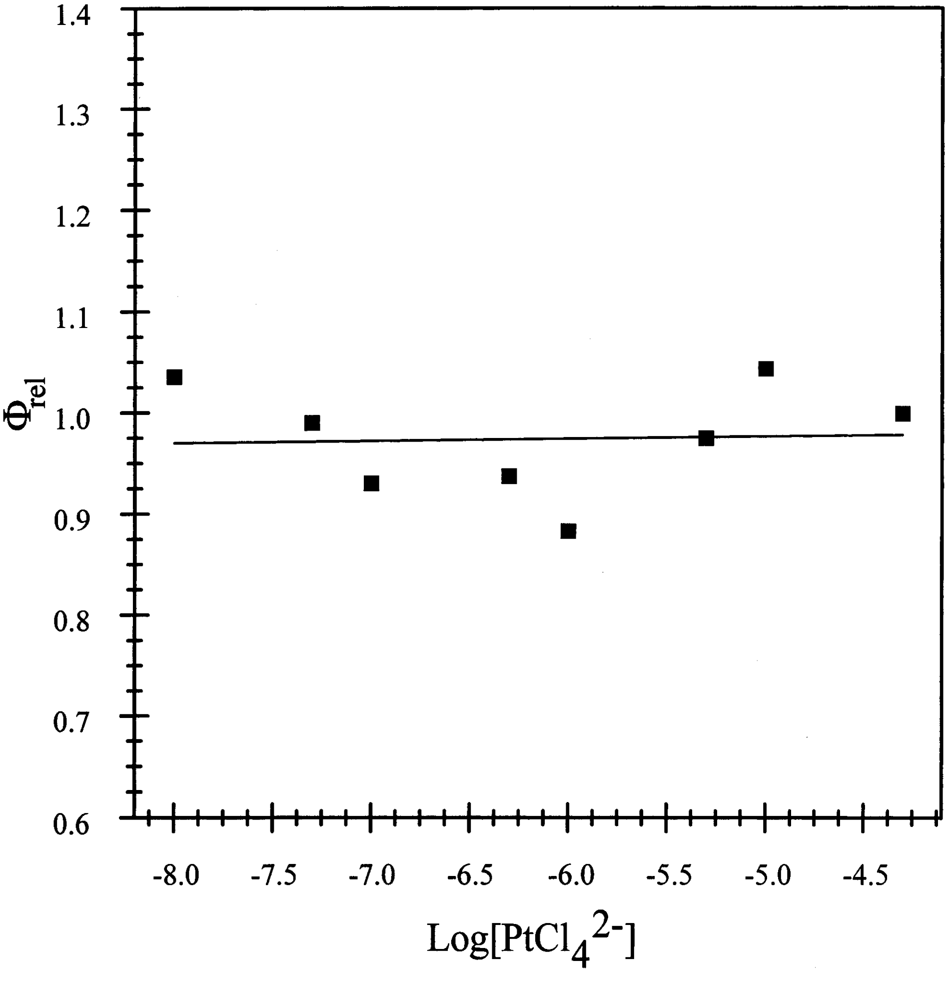

Fig. 2. The effect of added $PtCl_4^{2-}$ on the quantum yield of formation of the bimetallic $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$.

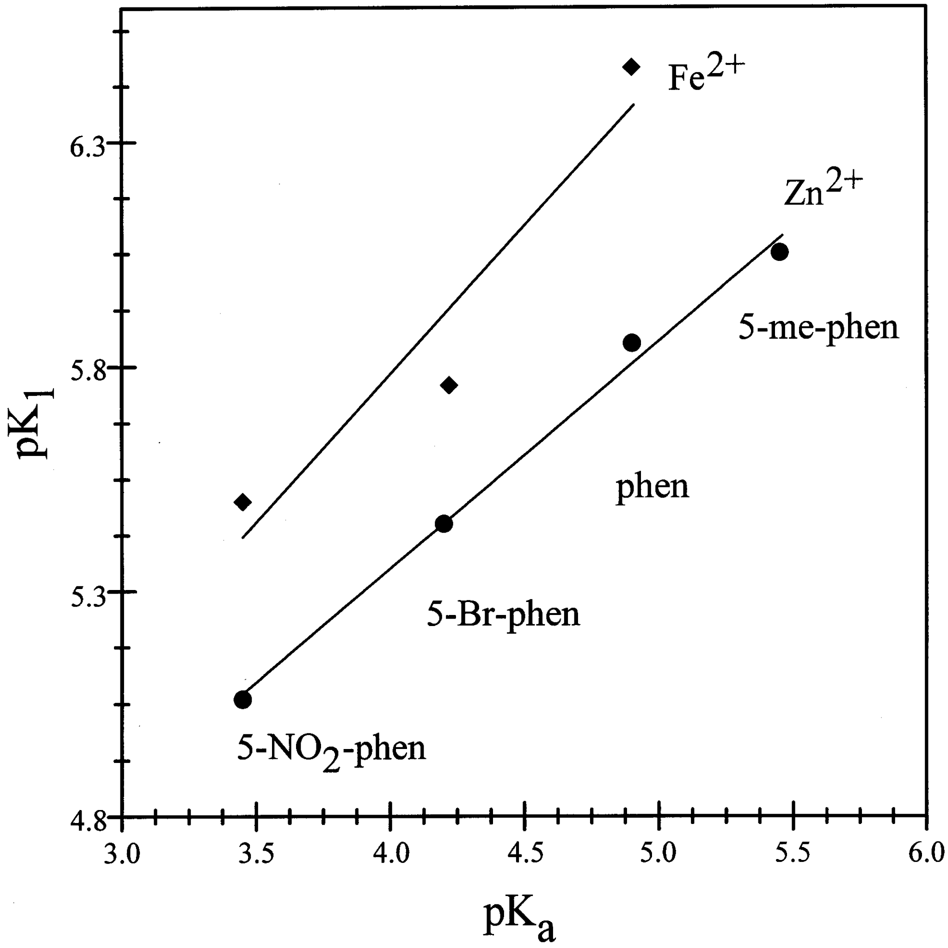

Fig. 3. The dependence of the equilibrium constant for coordination of different phenanthrolines onto Fe(II) and Zn(II) on the pK_a of the ligand.

these bimetallic complexes. The MLCT state of $(bpy)_2Ru(dpp)^{2+}$ is localized on the dpp ligand, and increased electron density increases the basicity of at least one of the peripheral nitrogens by $\geq 10^6$ [3,4]. Brønsted basicity is not a universal indicator of coordinating ability, but within different series of similar ligands, the equilibrium constant for coordination of the ligand, K, is directly proportional to the Brønsted basicity of the coordinating ligand. The equilibrium constant for the coordination of a number of substituted phenanthrolines onto Fe^{2+} (Fig. 3) is given by the relation $\log K_1 = 0.596\, pK_a + 2.93$ [54]. Although the individual constants A and B differ, equilibrium constants for coordination of a variety of ligands onto a number of different metals are described by relations of the general form

$\log K_1 = A\,\mathrm{p}K_a + B$ [55]. Hence, we propose that the increase in electron density at the peripheral nitrogens, signaled by the immense increase in Brønsted basicity, results in an excited-state Lewis acid–base chemistry where changes in coordination, rather than energy or electron transfer, leads to coordination of the second metal ion. Optical excitation of $(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+}$ increases the basicity of one of the peripheral nitrogens, thought to be the pyrazine nitrogen [3], by 6.45 pK units which, according to the above relationship, increases the equilibrium constant for coordination of the second metal by ca. 6×10^3.

Optical excitation increases electron density at one of the peripheral nitrogens, and we propose that this increased electron density enhances coordination to the hexachloride. Since the increased electron density at the peripheral nitrogens exists only in the excited state, however, the initial interaction

$$^*(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+} + \mathrm{MCl}_6^{n-} \rightarrow [^*(\mathrm{bpy})_2\mathrm{Rudpp{-}MCl}_6]^{4-n} \qquad (2)$$

is viewed as the formation of an $[^*(\mathrm{bpy})_2\mathrm{Rudpp{-}MCl}_6]^{4-n}$ exiplex [1,2]. Exiplex formation with Ru(II) diimines occurs between Ag^+ and $^*\mathrm{Ru(bpz)}_3^{2+}$ [56] and $^*\mathrm{Ru(bpy)}_3^{2+}$ [57], as well as between Lewis bases and Cu(I) phenanthrolines [58] and the complexes of late transition metal ions [59]. In latter case, the reduced emission intensity and the shift to longer wavelength are attributed to the formation of $[^*\mathrm{Ru(bpy)}_3^{2+}{-}\mathrm{Ag}^+]$ and $[^*\mathrm{Ru(bpy)}_3^{2+}{-}\mathrm{Ag}_2^+]$ exiplexes, while $^*\mathrm{Ru(bpz)}_3^{2+}$ exhibits similar spectral changes indicative of the formation of exiplexes of up to six Ag^+ per $^*\mathrm{Ru(bpz)}_3^{2+}$. Neither system, however, leads to a net chemical change. Adding Ag^+ to $(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+}$ produces identical changes in the emission spectrum, i.e. a reduction in emission intensity and a shift of the maximum to longer wavelength. Unlike the $\mathrm{Ru(bpy)}_3^{2+}{-}\mathrm{Ag}^+$ and $\mathrm{Ru(bpz)}_3^{2+}{-}\mathrm{Ag}^+$ systems, where there is no ground state interaction, $(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+}$ reacts thermally with Ag^+. Absorption spectra show that, within the time of mixing, the 470 nm maximum of Ru(II) → dpp π^* MLCT absorption shifts to 475 nm. This is in the direction expected for coordination of Ag^+ onto the peripheral dpp nitrogen of $(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+}$, but the extent of the shift, ca. 225 cm^{-1}, is less than that found with PtCl_6^{2-}, 2290 cm^{-1}; RhCl_6^{3-}, 769 cm^{-1} and PdCl_6^{2-}, 1139 cm^{-1}.

Since PtCl_6^{2-} reacts thermally with $(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+}$, the initial $^*(\mathrm{bpy})_2$-$\mathrm{Rudpp{-}MCl}_6$ interaction might not be viewed as the formation of an exiplex. Rather, excitation enhances an interaction that already occurs between the ground state molecules, as opposed to initiating an interaction that does not occur in the ground state. We believe the interaction should be referred as an exiplex to emphasize the point that excitation facilitates the formation of the bimetallic relative to the ground state. Furthermore, if the $\mathrm{p}K_a^*$ of $^*(\mathrm{bpy})_2\mathrm{Ru(dpp)}^{2+}$ is taken as a thermodynamic parameter, then according to the above relation, optical excitation increases the equilibrium constant for coordination by ca. 6×10^3 relative to the ground state. The enhanced interaction exists only in the excited state, and a secondary thermal event must occur to produce the observed thermodynamically stable bimetallic product. We propose that this secondary event arises from the chelate effect, i.e. the peripheral pyridine nitrogen on dpp binds competitively with relaxation of the excited state, and this secondary thermal event results in emission quenching and formation of a thermodynamically stable bimetallic complex [1,2].

This type of photochemical reaction is referred to as associative since the excited complex 'associates' with another to produce a product of higher metal content. Dissociative designates the converse where excitation facilitates the dissociation of the polymetallic complex. As noted above, the $\geq 10^5$ reduction in the basicity that accompanies population of the MLCT state of *cis*-Ru(bpy)$_2$(CN)$_2$ signals a significant reduction in electron density at the cyano group. Assuming the reduction in electron density also translates into a change in coordinating ability in analogous manner to that for the above associative process led us to suggest that excitation of the bimetallic (bpy)$_2$Ru(CN)(μ-CN)Rh(NH$_3$)$_4$Br^{2+} leads to a dissociative excited state where the dissociated fragments exist within the solvent cage, [(bpy)$_2$Ru(CN)$_2$Rh(NH$_3$)$_4$Br^{2+}] [2]. In this case, relaxation to the ground state returns the electron density to the cyano ligands, and provided the molecular fragments have not escaped from the solvent cage the dissociated fragments recombine to form the bimetallic. As with an excited state electron transfer, a secondary thermal reaction must occur to result in a net chemical change.

Considerable work remains to establish these mechanistic ideas, but the photoinduced formation of a bimetallic, the pH dependence of the quantum efficiency of dissociation of (bpy)$_2$Ru(CN)(μ-CN)Rh(NH$_3$)$_4$Br^{2+}, and the formation of exiplexes even under conditions where oxidative quenching of the excited complex is highly exergonic, leads us to believe that the chemistry of the MLCT states of Ru(II) diimines is not limited to energy and electron transfer.

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