

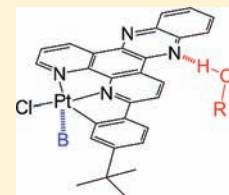
Regiospecific Quenching of a Photoexcited Platinum(II) Complex at Acidic and Basic Sites

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Supporting Information

ABSTRACT: The carbometalated complex Pt(dppz ϕ^*)Cl, where dppz ϕ^* denotes the 6-(4-*tert*-butylphenyl)-dipyrido[3,2-*a*:2',3'-*c*]phenazine ligand, exhibits emission in a dichloromethane solution at room temperature with a concentration-dependent excited-state lifetime. Extrapolation to zero Pt(dppz ϕ^*)Cl concentration yields a limiting lifetime of 11.0 μ s in the absence of dioxygen along with an impressive emission quantum yield of 0.17. The visible absorption of Pt(dppz ϕ^*)Cl has intraligand charge-transfer as well as metal-to-ligand charge-transfer character, but the oscillator strength may derive, in part, from π - π^* excitation within the phenazine moiety. An intriguing aspect of the Pt(dppz ϕ^*)Cl system is that its reactive excited state is subject to regiospecific quenching by Lewis bases and hydrogen-bonding Lewis acids. Base-induced quenching involves an attack at the platinum center. The rate constant increases with the donor strength of the quencher and reaches the order of 10^8 $M^{-1} s^{-1}$ with a relatively strong base like dimethyl sulfoxide. The orbital parentage of the excited state probably influences the quenching rates by affecting the charge density at platinum, as well as at the phenazine nitrogen atoms, where attack by Lewis acids occurs. With mildly acidic alcohols like 1,1,1,3,3,3-hexafluoropropan-2-ol and 2,2,2-trifluoroethanol, high concentrations of the quencher are necessary to suppress the emission. Carboxylic acids are stronger quenchers, and the quenching constant increases with the acid strength according to tabulated pK_a values. Cyanoacetic acid exhibits the highest measured quenching rate constant (2.6×10^9 $M^{-1} s^{-1}$), which only decreases 30% when the acid is in the (NC)CH₂CO₂D form. A weaker acid, CH₃CO₂H, exhibits an even smaller kinetic isotope effect. Literature comparisons suggest that acid-induced quenching probably involves hydrogen-bond formation as opposed to net proton transfer.



INTRODUCTION

Several groups have successfully detected the proton and/or other Lewis acids using a platinum(II) complex as the reporting agent.¹ In most designs, one of the ligands bound to platinum incorporates a basic atom such as nitrogen or a covalently attached chelating function on the periphery. Luminescence-based detection is possible whenever binding of a Lewis acid induces a spectral shift or switches the emission signal on or off. Furthermore, the quenching mechanism can be either dynamic or static. Because of rate limitations, a static mechanism is probably more appropriate for uptake of a metal ion that chelates to the reporter. On the other hand, dynamic quenching is certainly feasible if the process involves simple hydrogen bonding or attack of the proton at a specific atomic center. If the sensor complex provides more than one type of reaction center, the quenching may be regiospecific as well. Platinum(II)-containing luminophors are intriguing in this regard because they can be subjected to quenching by Lewis bases.^{1d,2} Not just platinum but other late-transition-metal ions tend to support quenching by Lewis bases via exciplex formation because the metal center often has open coordination sites that allow access to frontier orbitals.^{1d,2,3} A platinum(II) complex involving a suitable polypyridine ligand and a low-lying metal-to-ligand charge-transfer (MLCT) excited state should, in principle, be capable of providing a sensing capability for Lewis acids as well as Lewis bases. On the one hand, MLCT excitation should facilitate a nucleophilic attack at the metal center, by virtue of the increase in the formal oxidation state of platinum. Transferring an electron to

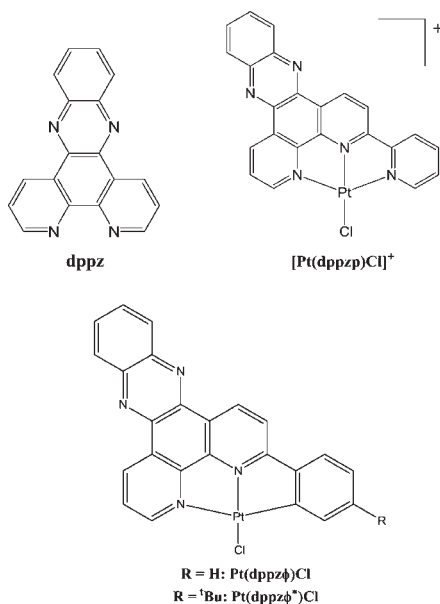
the ligand should, on the other hand, enhance the reactivity of basic sites positioned on the ligand periphery. One caveat is that platinum is a third-row transition metal with a high ligand-field stabilization energy, so there may well be a kinetic barrier that hinders the rate of ligand uptake.² Another mitigating effect is that the pure MLCT orbital parentage is very rare for the lowest-energy excited state of a platinum(II) complex because platinum(III) is not a very stable oxidation state.^{1d}

With regard to acid sensing, the dipyrido[3,2-*a*:2',3'-*c*]phenazine ligand (dppz in Scheme 1) is a classic ligand system compatible with many different metal ions.⁴ The most famous derivative is the [Ru(bpy)₂(dppz)]²⁺ system (bpy denotes 2,2'-bipyridine), which functions as a DNA "light switch".^{4b,5} The π system of the dppz ligand naturally bifurcates in such a way that the complex exhibits two distinct kinds of low-lying MLCT states. One is an emissive state, wherein the excitation localizes on the bpy part of the dppz ligand, adjacent to the metal center. The other is a dark state, in which the excitation localizes on the complementary phenazine (phz) moiety, distal to the metal center.⁶ Several groups have investigated dppz complexes of platinum; however, there is not much information available about acid-related quenching.⁷ The reason may be that the emissive excited state apparently exhibits triplet intraligand (³IL), as opposed to ³MLCT, orbital parentage.^{7b,c} Recently, our group and others have begun investigating a tridentate

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Scheme 1



analogue of the dppz ligand, namely, 6'-(2''-pyridyl)-dipyrido[3,2-*a*:2',3'-*c*]phenazine or dppzp (Scheme 1).⁸

The dppzp ligand differs from dppz in some important ways. For example, presumably because of a more delocalized, less bifurcated π system, studies reveal that the dppzp ligand is less prone to forming dark MLCT states.⁹ In the same study involving $[\text{Ru}(\text{dppzp})(\text{bpy})\text{CN}]^+$, Stewart et al. nevertheless, demonstrated that dppzp complexes are still capable of proton sensing (DNA “light switch” behavior). McGuire et al. have also studied the $[\text{Pt}(\text{dppzp})\text{Cl}]^+$ complex and concluded that the complex exhibits $^3\pi-\pi^*$ (phz) emission in a dichloromethane (DCM) solution.^{8b} Consistent with a lack of charge-transfer (CT) character, introducing acetic acid into the solution gave no sign of emission quenching. The analogous platinum(II) complex of the 6-phenyldipyrido[3,2-*a*:2',3'-*c*]phenazine or dppz ϕ ligand (Scheme 1) proved more promising in that acetic acid acts as a quencher; however, the $\text{Pt}(\text{dppz}\phi)\text{Cl}$ complex is very poorly soluble in common solvents.^{8b} A more soluble carbometalated form, $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$, where dppz ϕ^* denotes the 6-(4-*tert*-butylphenyl)dipyrido[3,2-*a*:2',3'-*c*]phenazine ligand (Scheme 1), is the focus of the present report. The emissive excited state of the complex lives for microseconds in a DCM solution and is subject to quenching by Lewis bases as well as Lewis acids such as alcohols and carboxylic acids. Isotopic labeling studies reveal that a hydrogen-bonding interaction with the excited state, as opposed to proton transfer, is responsible for the acid sensitivity.

EXPERIMENTAL SECTION

Materials. Ligand precursors and most chemicals including K_2PtCl_4 , quenching solvents, $\text{CH}_3\text{CO}_2\text{D}$, CH_3OD , and *o*-dichlorobenzene came from Sigma-Aldrich in sufficiently pure form for use as received. Deuterated chloroform came from Cambridge Isotope Laboratories. Distillation from sodium/benzophenone afforded anhydrous tetrahydrofuran (THF). Mallinckrodt was the supplier of all additional solvents. The vendor for silica gel was Fisher Scientific. The coumarin 440 laser dye and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ were products of Exciton and the G. Fredrick Smith Chemical Company, respectively.

Synthetic Methods. (4-*tert*-butylphen-6-yl)dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz ϕ^*). The synthesis, modeled after the method of Sauvage and co-workers,¹⁰ began with the preparation of the lithium reagent by the dropwise addition of 1.5 equiv of *n*-butyllithium to a flask containing *p*-*tert*-butylbromobenzene in 25 mL of anhydrous THF at -78°C under nitrogen. Subsequent steps included transfer of the solution via a cannula needle to a -78°C THF solution containing 1.0 equiv of dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz),¹¹ stirring for at least 30 min, gradual warming to room temperature, followed by stirring for another 5 h, subsequent quenching with methanol, and finally evaporation of the solvent. After dissolution of the resulting oil in DCM, treatment with excess MnO_2 for 12 h rearomatized the ligand, and filtration through Celite removed particulates. Elution of the product from alumina with 50% THF in hexanes provided for the removal of unreacted dppz. Elution from a silica column with 10% ethyl acetate in DCM yielded the analytically pure product. Overall yield: 25%. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_4$: C, 81.13; H, 5.59; N, 13.52. Found: C, 80.98; H, 5.59; N, 13.12.

$\text{Pt}(\text{dppz}\phi^*)\text{Cl}$. Refluxing a mixture of 50 mg (0.12 mmol) of dppz ϕ^* and 43.5 mg (0.105 mmol) of K_2PtCl_4 in 50 mL of glacial acetic acid for 24 h yielded a dark-orange solution and a crude product in the form of a precipitate. The initial workup involved vacuum filtration and washing with water and diethyl ether. Recrystallization from DCM and hexanes afforded the analytically pure product. Yield: 40 mg (90%). Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{N}_4\text{ClPt} \cdot 2\text{H}_2\text{O}$: C, 49.45; H, 3.71; N, 8.24. Found: C, 49.57; H, 3.66; N, 8.01.

(4-*tert*-butylphen-2-yl)-1,10-phenanthroline (ph ϕ^*). Analogous procedures yielded the ph ϕ^* ligand and the corresponding platinum complex $\text{Pt}(\text{ph}\phi^*)\text{Cl}$. Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{ClN}_2\text{Pt}$: C, 48.76; H, 3.53; N, 5.17. Found: C, 48.57; H, 3.97; N, 4.87. The agreement between the absorption and excitation spectra of the complex also attested to the purity of the sample. See the Supporting Information.

General Methods. Galbraith Laboratories performed the microanalyses. For spectral studies, the sample preparation involved standard volumetric methods. The solvent was typically spectral-grade dichloromethane (DCM). Measuring the kinetic isotope effect (KIE) with cyanoacetic acid was possible using anhydrous DCM containing 0.1 M methanol-*d* as the solvent to provide for exchange of the acidic proton. Control experiments established that exchange of the OH proton is facile even on the NMR time scale. Thus, a sample of cyanoacetic acid gave an OH resonance at $\delta = 4.5$ ppm, whereas the OH resonance for MeOH came at $\delta = 1.5$ ppm in deuterated DCM. When the sample contained 20 mM acid and 100 mM MeOH, the spectrum showed an average OH resonance signal at $\delta = 3.1$ ppm. Finally, the corresponding resonance shifted to $\delta = 3.8$ ppm when the sample contained 20 mM cyanoacetic acid and 100 mM MeOD. The cuvette path length was 2 cm for absorbance measurements pertaining to determination of the molar absorptivity. During the quantum yield measurement, the method used for the removal of dioxygen was sparging with a stream of solvent-saturated argon or dinitrogen gas for at least 10 min in a screw-cap cell sealed with a septum. The excitation wavelength was 435 nm for lifetime measurements, and in the quenching runs, a Stern–Volmer plot¹² of $1/\tau$ versus the concentration of the complex yielded the rate constant and the limiting lifetime τ_0 . For the weakest Lewis acids, the kinetics exhibited a term that was second-order in the quencher concentration. In those trials, eq 1 described the pseudo-first-order decay constant:

$$k = k_0 + k_q[\text{Q}] + k_q'[\text{Q}]^2 \quad (1)$$

where $k_0 = 1/\tau_0$ is the decay constant at a fixed platinum concentration in the absence of Lewis acid while k_q and k_q' describe terms that are dependent on the quencher concentration. The conditions were ambient, and a 475-nm-long pass emission filter isolated the signal from the complex of interest. In the acid- and base-quenching studies, the platinum complex concentration remained constant within the range of 7–10 μM .

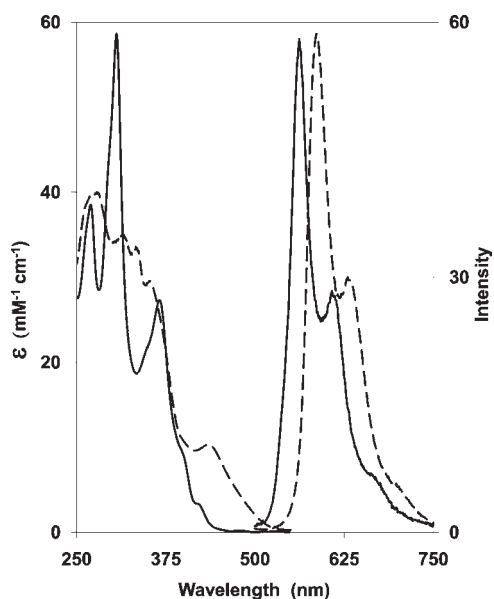


Figure 1. Left: absorption spectra of $[\text{Pt}(\text{dppz})\text{Cl}]^+$ (solid) and $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ (dashed) in a DCM solution at room temperature. Right: corresponding emission spectra in the same medium.

The method of Parker and Rees allowed for estimation of the emission quantum yield,¹³ with $[\text{Ru}(\text{bpy})_3]^{2+}$ dissolved in acetonitrile as a standard ($\phi = 0.062$).¹⁴

In the electrochemical studies, the electrolyte solution was 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) dissolved in dimethylformamide (DMF). The working electrode was glassy carbon, and the auxiliary electrode was platinum mesh. A silver/silver nitrate electrode containing 3 M aqueous potassium chloride was the reference electrode for the cyclic voltammetry measurements of the free ligand. In the square-wave voltammetry studies of the platinum complex, the reference electrode consisted of a silver wire immersed in acetonitrile containing 0.01 M silver nitrate. Calibration against the ferrocene/ferrocenium couple monitoring under each set of conditions makes comparisons possible.

Instrumentation. The absorption spectrophotometer was a Varian Cary 100 Bio instrument, and the spectrofluorimeter was a Varian Cary Eclipse instrument equipped with a R3896 phototube. The light source for lifetime measurements was a VSL-337-NDS nitrogen dye laser from Laser Science coupled with a DLM-220 dye component. The detection system included a Hamamatsu R928 phototube, a Pacific Instruments model 277 high-voltage supply, and a Tectronix TDS 520 digitizing oscilloscope. The NMR spectrometer was a Varian Inova 300. The potentiostat used in the square-wave studies was a Princeton Applied Research Parstat 2273 in combination with Power Pulse software and a Lauda Ecoline star edition temperature controller. A CHI-620 electrochemical analyzer (CH Instruments) provided the cyclic voltammetry data.

RESULTS

Spectral Studies. The $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ complex is only sparingly soluble in common organic solvents, but the solutions obtained are adequate for physical studies. Moreover, the complex has considerably better solubility properties than the previously studied $\text{dppz}\phi$ analogue, for which the most practical solvent was 2-chloronaphthalene.^{8b} At saturation in DCM, the concentration of the $\text{dppz}\phi^*$ complex is on the order of 25 μM . In a DCM solution, the electronic absorption spectrum of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ exhibits a series of absorption bands between 250 and 400 nm that nominally represent intraligand $\pi-\pi^*$ transitions (Figure 1). A CT band appears at 435 nm and

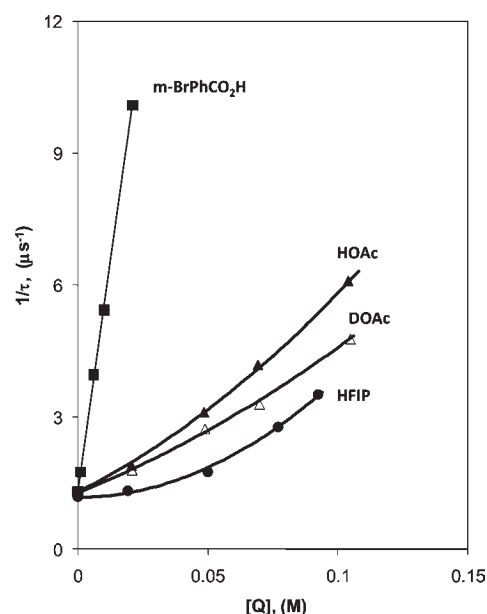


Figure 2. Stern–Volmer plots for quenching of photoexcited $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ in DCM by *m*-bromobenzoic acid (■), $\text{CH}_3\text{CO}_2\text{H}$ (▲), $\text{CH}_3\text{CO}_2\text{D}$ (△), and HFIP (●). See Table 1 for the parameters used for the calculated lines. For each plot, the platinum concentration is constant, and the atmosphere in the cuvette is air.

shifts to longer wavelengths in toluene (442 nm) and *o*-dichlorobenzene (448 nm). Because the absorbance at 435 nm follows Beer's law behavior consistent with an extinction coefficient of 10 300 $\text{M}^{-1} \text{cm}^{-1}$, the complex almost certainly exists as a single monomeric species in a DCM solution.

Figure 1 also presents the emission spectrum of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ in DCM, and the peaks fall at about the same wavelengths in other solvents. The emission decays with a rate that varies with the concentration of the complex. Indeed, a Stern–Volmer analysis reveals that ground-state $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ acts as a quencher with a second-order rate constant of $k_q = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The excited-state lifetime is concentration-dependent as well, and extrapolation of the Stern–Volmer plot to zero $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ concentration yields a limiting lifetime of 11.0 μs in a deoxygenated DCM solution. The corresponding extrapolated quantum yield for emission is 0.17.

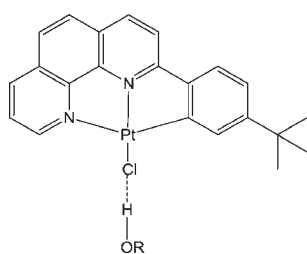
Quenching by Lewis Acids. Acetic acid is not an effective quencher for photoexcited $[\text{Pt}(\text{dppz})\text{Cl}]^+$, so it is a good test case for the initial quenching studies of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$.

Acetic acid turns out to be a modest quencher of the carbonylmetalated $\text{dppz}\phi^*$ complex. Also, for acetic acid as well as some other quenchers, the Stern–Volmer plot reveals that the rate law exhibits both first- and second-order dependences on the quencher concentration. See Figure 2 for representative data. The $k_q = 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ term, which is first-order in acetic acid, is about 7 times smaller than the previous value reported for $\text{Pt}(\text{dppz}\phi)\text{Cl}$ in 2-chloronaphthalene.^{8b} With the $\text{dppz}\phi^*$ complex, the quenching constant generally increases with the strength of the carboxylic acid, as measured by the apparent $\text{p}K_a$ (Table 1). The fluorinated alcohols 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) and 2,2,2-trifluoroethanol (TFE) also act as weak quenchers.

As is evident in Table 1, a pathway that is second-order in the acid concentration comes into play for the weaker quenchers, and the explanation may be relatively straightforward. Thus, in their studies of alcohols interacting with $[\text{Ru}(\text{phen})_2\text{dppz}]^+$,

Table 1. Quenching of Pt(dppz ϕ^*)Cl by Lewis Acids in DCM at Room Temperature

quencher	pK _a ¹⁵	k _q , M ⁻¹ s ⁻¹	k _q ', M ⁻² s ⁻¹
(NC)CH ₂ CO ₂ H	18	2.6 × 10 ⁹	
ClCH ₂ CO ₂ H	18.8	2.6 × 10 ⁹	
<i>m</i> -BrPhCO ₂ H ^a	19	4.2 × 10 ⁸	
CH ₃ CO ₂ H	22.3	3.0 × 10 ⁷	1.6 × 10 ⁸
(NC)CH ₂ CO ₂ D	(18)	1.8 × 10 ⁹	
CH ₃ CO ₂ D	(22.3)	2.7 × 10 ⁷	9.5 × 10 ⁷
HFIP			3.8 × 10 ⁸
TFE			2.3 × 10 ⁵

^a *m*-Bromobenzoic acid.**Scheme 2**

Olofsson et al. have argued that the formation of a dark state depends upon the formation of separate hydrogen bonds to each nitrogen of the phz moiety.¹⁶ In that regard, it is worth noting that the first-order term is not even necessary for modeling of the quenching kinetics for Pt(dppz ϕ^*)Cl reacting with HFIP or TFE (Table 1). Transition states involving two molecules of quencher undoubtedly assemble in a stepwise manner because ternary collisions are so improbable. In fact, the assembly process may well begin in the ground state. However, hydrogen bonding of HFIP to a remote phz nitrogen atom of the dppz ϕ^* complex would *not* lead to the observed hypsochromic shift from 435 to 428 nm in the CT absorption maximum. A more likely explanation for the spectral shift is hydrogen-bond formation to the chloride coligand. Indeed, experiments reveal that the introduction of TFE induces a similar shift in the CT band of Pt(ph ϕ^*)Cl, which does not include a phz moiety; see Scheme 2. By the same token, association with TFE has no effect on the lifetime of the Pt(ph ϕ^*)Cl complex. Another observation worth noting is that the CT absorption of Pt(dppz ϕ^*)Cl does *not* shift with the addition of carboxylic acids, even though they are stronger Lewis acids. Presumably, the difference is that carboxylic acids preferentially self-associate in noncoordinating solvents to give cyclic, dihydrogen-bonded adducts.¹⁷

The other interesting observation regarding quenching by carboxylic acids is the very small deuterium isotope effect. With cyanoacetic acid as the quencher, the data in Table 1 reveal that $k_H/k_D = 1.4$, while with acetic acid as the quencher, the corresponding ratio is 1.1.

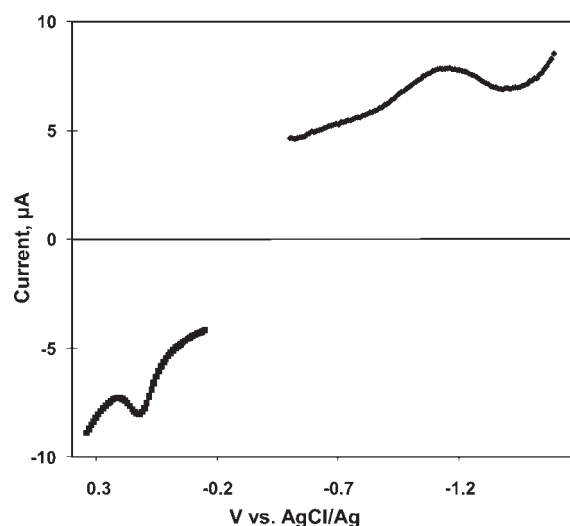
Quenching by Lewis Bases. Lewis bases are also capable of quenching the emission of a platinum polypyridine complex, but the point of attack is at an open coordination site of the metal center rather than on the polypyridine ligand. Table 2 contains a summary of the quenching constants obtained with a series of Lewis bases interacting with [Pt(dppzp)Cl]⁺ or Pt(dppz ϕ^*)Cl.

Table 2. Quenching Constants Obtained with Lewis Bases in DCM

quencher	DN ^a	k _q , M ⁻¹ s ⁻¹	
		[Pt(dppzp)Cl] ⁺ ^{8b}	Pt(dppz ϕ^*)Cl
MeCN	14.1	3.0 × 10 ⁶	N.A.
Acetone	17	5.0 × 10 ⁶	2.1 × 10 ⁵
THF	20	1.0 × 10 ⁷	6.0 × 10 ⁶
DMF	26.6	6.0 × 10 ⁷	1.0 × 10 ⁷
DMSO	29.6	N.A.	1.0 × 10 ⁸

^a Donor number.¹⁸**Table 3. Reduction Potential in DMF Containing 0.1 M TBA[PF₆]**

species	E ^o , vs Fc ^{+ / 0}	species	E ^o , vs Fc ^{+ / 0}
dppzp	-1.59 ^{8b}	dppz ϕ^*	-1.61
[Pt(dppzp)Cl] ⁺	-0.96 ^{8b}	Pt(dppz ϕ^*)Cl	-1.27
[Ru(dppzp)(bpy)CN] ⁺	-1.34 ⁹	dppz	-1.6 ¹⁹
[Ru(dppzp) ₂] ²⁺	-1.23 ^{8a}	[Ru(bpy) ₂ (dppz)] ²⁺	-1.36 ²⁰

**Figure 3.** Square-wave voltammograms of ferrocene (left) and Pt(dppz ϕ^*)Cl (right). The temperature is 53 °C, and the solvent is DMF containing 0.1 M TBAH.

In each case, the quenching rate constants are modest, with values on the order of 10⁷ M⁻¹ s⁻¹. For a given base, the quenching constant is 2–4 times smaller for Pt(dppz ϕ^*)Cl as opposed to [Pt(dppzp)Cl]⁺. An empirical ordering of the base strength is available in the form of the Gutmann donor numbers (DNs).¹⁸ The correlation between the DN and the measured quenching constants compiled in Table 2 reveals that significant quenching of the photoexcited state of the carbometalated dppz ϕ^* complex requires the use of relatively strong bases, those with DN ≥ 20.

Electrochemistry. Even at saturation and elevated temperature, the concentration of Pt(dppz ϕ^*)Cl dissolved in DMF is too low for standard cyclic voltammetry studies. However, square-wave voltammetry on a saturated solution of the complex yields a reduction peak at -1.27 V vs ferrocene (Table 3) at temperatures of 37 and 53 °C (Figure 3). To obtain currents of similar

magnitude from the sample and reference, the anodic wave in Figure 3 pertains to a very dilute solution of ferrocene. The juxtaposition of the two responses reveals that the wave from ferrocene is noticeably narrower than that of the $\text{dppz}\phi^*$ complex.

DISCUSSION

The electrochemistry data are critical to understanding the observed quenching processes. Data in Table 3 indicate that free dppz , dppzp , and $\text{dppz}\phi^*$ undergo reductions at almost the same potential, which corresponds to reduction of the catacondensed phz domain within each ligand. Complexed forms of the ligands are much easier to reduce; however, in a dppzp complex, the π molecular orbital involved in the reduction process no longer exclusively resides on the phz moiety. One indication is that the first reduction of $[\text{Ru}(\text{dppzp})_2]^{2+}$ occurs at a *less* cathodic potential than that of $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$. Studies of the related $[\text{Ru}(\text{dppzp})(\text{bpy})\text{CN}]^+$ system point to a similar conclusion, in that Stewart et al. have found that the lowest-energy MLCT excited state of the complex is emissive.⁹ If excitation were strictly localized on the distal phz portion of the ligand, one would expect the state to be nonemissive.^{6a} Interestingly, the results in Table 3 show that the dppzp ligand is even easier to reduce when it coordinates to platinum as opposed to ruthenium. In their studies of platinum terpyridine complexes, Gray and co-workers have rationalized the effect in terms of a mesomeric interaction involving the empty $6p_z$ orbital of platinum. From this point of view, delocalization of the π^* system of the ligand onto platinum is the stabilizing influence facilitating reduction of the coordinated ligand.²¹ Note that in a six-coordinate complex the effect all but vanishes because the p_z orbital of the metal preferentially becomes involved in σ bonding with two additional ligands. In that light, one should also consider the inductive effect of the metal center because coordinate covalent bond formation effectively shifts the positive charge from the metal center onto the ligand and thereby facilitates ligand reduction. For a given ligand, the effect is larger for a platinum(II) center simply because a ruthenium(II) complex has more coligands. The inductive effect of a formally carbanionic coligand goes in the opposite direction, of course. Thus, Sauvage and co-workers have shown that a carbometalating ligand induces a *cathodic* shift in the reduction potential of a neighboring ligand.²² The same forces naturally apply to the more reducible side of the $\text{dppz}\phi^*$ ligand itself and account for the ca. 300 mV shift to the more negative potential required for the reduction of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ versus $[\text{Pt}(\text{dppzp})\text{Cl}]^+$.

The comparatively broad square-wave signal obtained from the $\text{dppz}\phi^*$ complex merits further comment. A broadened wave can certainly be the consequence of a kinetic barrier to electron transfer at the electrode. However, that is not likely to be the case here because reduction takes place at the aromatic ligand, which implies a minimal change in structure. A more likely interpretation assumes an ECE response, which involves a coupling of electrochemical and chemical processes, as reported by Field et al. for a related system.²³ Their studies involved a phenylterpyridine complex of platinum(II), abbreviated here as $[\text{LPtCl}]^+$. One-electron reduction led to association with an unreduced complex to give a $[\text{LPtCl}]_2^+$ species, which underwent reduction at a marginally more negative potential and effectively broadened the wave obtained in the cyclic voltammogram. Unfortunately, solubility problems prevent a more detailed investigation of the

electrochemistry of the $\text{dppz}\phi^*$ complex, but it is worth mentioning that Field et al. also deduced that the ECE mechanism tends to arise with “flat” platinum(II) complexes that have ligands with extended π systems because of their propensity to engage in stacking interactions.²³ By that criterion, the $\text{dppz}\phi^*$ complex is an obvious candidate for the process.

Absorbance. Figure 1 presents the absorption spectrum of $[\text{Pt}(\text{dppzp})\text{Cl}]^+$, which more or less unfolds as a series of regiospecific excitations. The intense band occurring around 290 nm is largely a $\pi-\pi^*$ transition of the trpy component found in the dppzp ligand, while the absorption that occurs in the vicinity of 370 nm is ascribable to the phz group within the ligand.^{8b,24} The comparatively weak, long-wavelength shoulder that appears around 420 nm is not present in the spectrum of the free ligand. Attribution of the long-wavelength band as a MLCT transition is plausible by analogy with the results reported for related platinum(II) polypyridine complexes.^{1d,25} The absorption spectrum of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ is qualitatively similar; however, there are some significant differences (Figure 1). More specifically, the intraligand absorption shifts to slightly higher energy and more evenly distributes over almost the entire near UV region of the spectrum. On the other hand, the CT excitation shifts to longer wavelength, and the intensity increases. By extension, one can assign the CT absorption of the carbometalated complex to MLCT excitation as well.²⁶ However, the CT absorption of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ is much more intense than that of $\text{Pt}(\text{php})\text{Cl}$, the complex, which is analogous to $[\text{Pt}(\text{dppzp})\text{Cl}]^+$ with 1,10-phenanthroline in place of the dppz core.²⁷ The difference in the absorption intensity is striking because the presence of the phz group has almost no impact on the relative CT absorption intensities of $[\text{Ru}(\text{trpy})(\text{bpy})\text{CN}]^+$ and $[\text{Ru}(\text{dppzp})(\text{bpy})\text{CN}]^+$, where trpy denotes 2,2':6',2''-terpyridine.⁹ The explanation may be that the CT absorption originates from an orbital with substantial ligand character in the case of the platinum wherein the metal(III) oxidation state is much less accessible.^{1d} A related effect occurs in iridium(III) systems, for which calculations suggest that the highest occupied molecular orbital (HOMO) orbital generally includes about 50% iridium character as well as a prominent contribution from the π system of the carbometalated phenyl group.²⁸ In fact, density functional theory calculations on the free $\text{Hdppz}\phi$ ligand have revealed that the HOMO delocalizes over the dppz group as well as the attached phenyl, while the lowest unoccupied molecular orbital resides mainly on the phz moiety.^{8b} On that basis, one would anticipate that the CT absorption of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ has mixed ILCT/MLCT character and that the oscillator strength derives, in part, from $\pi-\pi^*$ excitation within the dppz moiety.

Luminescence. In the case of $[\text{Pt}(\text{dppzp})\text{Cl}]^+$, the emitting state has mainly triplet $\pi-\pi^*(\text{phz})$ character.^{8b} The small magnitude of the radiative rate constant, ca. 600 s^{-1} , reveals that d-orbital participation in the excitation is minimal. The assignment of largely phz intraligand character follows from the fact that copper(I) and rhenium(II) complexes of the dppz ligand exhibit a virtually identical band shape.^{4c,e} In contrast, a number of observations suggest that the emitting state of $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ has a mixed-orbital parentage that involves at least some CT character. First, the emission from $\text{Pt}(\text{dppz}\phi^*)\text{Cl}$ occurs at longer wavelengths, and the radiative rate constant, calculated as the ratio of the emission quantum yield and the excited-state lifetime at infinite dilution, is 25 times greater at $1.5 \times 10^4 \text{ s}^{-1}$. The emission from the $\text{dppz}\phi^*$ complex is also subject to self-quenching, analogous to the MLCT emitting state of the phenyl-2,2'-bipyridine complex studied by Che and co-workers.²⁹ At the same time, the delocalized, intraligand character of the excitation

of Pt(dppz ϕ^*)Cl is evident from the fact that the emission shifts very little with a change in the solvent and the fact that the dppzp and dppz ϕ^* complexes exhibit similar band shapes including almost identical vibronic structure. Acid- and base-induced quenching studies described below shed additional light on the system.

Quenching by Lewis Acids. Ordinary alcohols like methanol are not effective at quenching the emission from Pt(dppz ϕ^*)Cl, but HFIP and TFE are weak quenchers. The same two alcohols also dynamically quench the fluorescence of fluorenone, and Linschitz and co-workers have ascribed the effect to hydrogen-bond formation at the ketonic oxygen, which becomes more basic in the excited state.³⁰ The idea is that coupling to the alcohol facilitates radiationless decay to the ground state by virtue of the fact that the O–H stretching vibration of the alcohol functions as a good accepting mode in the electronic-to-vibrational energy-transfer process. The alcohols must quench the emission of the dppz ϕ^* complex by a similar mechanism because quenching depends on the presence of the electron-withdrawing fluorine atoms, which enhance the hydrogen-bonding ability.³¹ In the case of the dppz ϕ^* complex, the interactions logically take place at phz nitrogen atoms because they take on negative charge in the excited state.^{8b} Consistent with a dynamic quenching process, there is no shift in the emission signal in the presence of alcohols.

In the context of the proposed quenching mechanism, it is not surprising that carboxylic acids are even stronger quenchers. The ability to act as a hydrogen-bond donor ought to correlate with the p*K_a*, and the quenching rate constant sensibly increases with the acid strength. With the carboxylic acidic quenchers, however, the question arises as to whether quenching involves a simple hydrogen-bonding interaction or proton transfer to the excited state. It would seem possible to answer the question by measuring KIEs, but there are a wide variety of interpretations of the KIE data in the literature. Thus, Gray and co-workers investigated the quenching of photoexcited ReO₂(py)₄⁺ by a series of acids in a pyridine (py) solution. They concluded that the mechanism involved hydrogen bonding to the oxo ligands, as opposed to proton-transfer quenching,³² despite the fact that quenching by H₂O was 7–8 times faster than that by D₂O. A KIE that large is quite compatible with cleavage of the O–H bond of the quencher in the transition state. Liu et al. later studied the same complex in acetonitrile.³³ Even though the results with NH₄⁺ and ND₄⁺ yielded a KIE of only ca. 2, they concluded that quenching involved proton transfer because the rate of quenching correlated nicely with the p*K_a* value of the quencher. Turro and co-workers carried out a similar quenching study of [Ru(phen)₂(dppz)]²⁺ in acetonitrile and also concluded that the process involved proton transfer to the reduced dppz ligand, despite KIE = 2.2 for quenching by H₂O versus D₂O.³⁴ Finally, in an earlier paper by Barton et al., the authors used similar KIE results to conclude that quenching occurred by vibrational deactivation via a hydrogen-bonding pathway.^{4b} For the Pt(dppz ϕ^*)Cl system, the KIE ratios are even smaller at 1.1 and 1.4 for acetic and cyanoacetic acids, respectively. In view of all of the available data, the most logical conclusion is that quenching of the dppz ϕ^* system occurs by a hydrogen-bonding interaction rather than proton transfer. Indeed, the solvation energies are apt to be very unfavorable for a net proton-transfer process in a medium as weakly polar as DCM. A final caveat is that, even when proton transfer is thermodynamically feasible, the first step along the reaction coordinate probably involves hydrogen-bond formation. If so, induced radiationless decay within the precursor

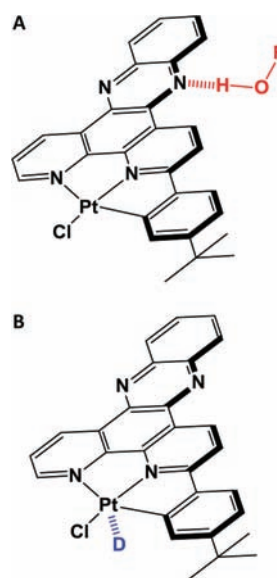


Figure 4. Plausible transition states for excited-state quenching of Pt(dppz ϕ^*)Cl via (A) hydrogen-bond formation at a phz nitrogen atom (hydrogen bonding to the chloride coligand may also occur but does not lead to quenching) and (B) coordinate covalent bond formation at platinum by electron-pair donor D.

complex may be fast enough to prevent completion of the proton-transfer process.

Quenching by Lewis Bases. Lewis bases are also capable of quenching the emission of platinum polypyridine complexes but via attack at the metal center. The electrophilicity of platinum naturally increases to the extent that the excitation has MLCT character and generates a formal increase in the oxidation state of platinum. In line with that argument, data compiled in Table 2 reveal that simple Lewis bases quench the emission of Pt(dppz ϕ^*)Cl and that the quenching constant increases with the base strength, as indicated by the Gutmann DN. The fact that the emitting state of Pt(dppz ϕ^*)Cl exhibits a significantly larger radiative rate constant in comparison to that of [Pt(dppzp)Cl]⁺ is also consistent with greater heavy-atom participation, and augmented MLCT character, in the excited state of the dppz ϕ^* complex. However, for any given base, the quenching constant is anywhere from 2 to 10 times larger for the excited state of the dppzp complex, which has mainly ³ π – π (phz) character. In addition, for the same bases, the corresponding quenching constants are as much as an order of magnitude larger with other platinum terpyridine complexes.³⁵ In aggregate, the data suggest that interpreting base-induced quenching in terms of a single factor, such as the percentage of MLCT character in the excited state, is an oversimplification.

CONCLUDING REMARKS

The Pt(dppz ϕ^*)Cl system undergoes novel regioselective quenching by hydrogen-bonding Lewis acids and electron-pair donors because of the changes in the electron density that accompany the formation of the emissive CT excited state (Figure 4). While there are many precedents for Brønsted acids altering the emission properties of platinum(II) polypyridine complexes, ligand protonation generally takes place in the ground state, as evidenced by clear changes in the absorption spectra.^{1a–e,36} The photoexcited Pt(dppz ϕ^*)Cl system is different in that ordinary hydrogen bonding

at the remote phz nitrogen atoms gives rise to dynamic quenching. Moreover, the base sensitivity stems from Lewis bases attacking at the platinum, as opposed to reversible protonation of a coordinated ligand.

Only a few reports have dealt with coordinate covalent bond formation in the excited state,^{2,35} whereas there are many reports of photoinduced Pt–Pt bond formation processes.³⁷ Some authors have noted that polar solvents can affect the lifetimes by unspecified k_{nr} paths,^{1a} but the present study clearly reveals how the donor strength can influence solvent-induced quenching. The quenching rates for Pt(dppz ϕ^*)Cl may vary with the degree of platinum(III) character in the excited state. However, the orbital parentage of the lowest-energy excited state may also change with the addition of a fifth ligand, as happens with copper(II)-containing porphyrins.^{3b,38} Another factor to consider with regard to base-induced quenching is the reorganization energy associated with adopting a five-coordinate structure. This term could be significant, especially in a system with a strongly binding, relatively rigid, carbometalating ligand like dppz ϕ^* . In view of all of the unknowns, the effort to understand how bond-formation processes affect the photophysical processes of platinum(II) polypyridines is still in the beginning phase.

■ ASSOCIATED CONTENT

S Supporting Information. Absorption spectra and Stern–Volmer plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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