Quenching Studies of the Excited State of (4,7-Diphenylphenanthroline)(1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolato)platinum(II), Pt(Ph_2phen)(ecda), by Aromatic Amines and Metallocenes and Determination of Its Excited-State Reduction Potential

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Rate constants for electron-transfer quenching of the lowest excited state of Pt(Ph_2phen)(ecda), where Ph_2phen is 4,7-diphenyl-1,10-phenanthroline and ecda is 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate, by a series of neutral amine quenchers have been determined. Also determined are the electron-transfer and energy-transfer quenching rates of the excited complex *Pt(Ph_2phen)(ecda) by a series of metallocene quenchers. The triplet states of the amine quenchers are relatively high in energy, >62 kcal/mol, compared to the triplet state of Pt(Ph_2phen)(ecda) at 52 kcal/mol so that electron transfer is the only possible pathway. However, the low triplet-state energies of the metallocene quenchers, 38–46 kcal/mol, permit energy transfer to compete with electron transfer in this system. Marcus analysis of the amine quenchers allows determination of the excited-state reduction potential, $E(\mathrm{Pt}^{*/-})$, of Pt(Ph_2phen)(ecda) at 0.93 V. $E(\mathrm{Pt}^{*/-})$ is also estimated using the ground-state reduction potential of Pt(Ph_2phen)(ecda) of −1.24 V vs SCE and the crossing point of the emission and excitation spectra of the complex at 2.22 V. This method of estimation yields a value of 0.98 V for $E(\mathrm{Pt}^{*/-})$ in agreement with the value obtained from the quenching studies. The correlation of $E(\mathrm{Pt}^{*/-})$ through the two methods allows estimation of $E(\mathrm{Pt}^{*/-})$ of related Pt(diimine)(dithiolate) complexes.

Introduction

Excited states of molecules have been shown to function as more powerful reductants and oxidants than their corresponding ground states.[1] This property is exploitable in net light-to-chemical energy conversion processes, as, for example, in the photochemical reactions of the excited complex $^*\mathrm{Ru(bpy)_3}^{2+}$ that lead to the reduction of protons to hydrogen in the presence of an electron-transfer quencher such as methyl viologen and a sacrificial donor such as triethanolamine.[2–15] The excited-state reduction and oxidation potentials of $\mathrm{Ru(bpy)_3}^{2+}$, which are important in the context of light to chemical energy conversion reactions, have been determined using different series of quenchers with variable strengths as reductants and oxidants.[16,17] Many other inorganic systems have been characterized by this approach as well, including $\mathrm{Cr(bpy)_3}^{3+}$ [18–21] and $\mathrm{Cu(Ph_2phen)_2}^{+}$ [22] among others.[23]

Recently, our laboratory reported the synthesis and electronic properties of a series of neutral Pt(diimine)(dithiolate) complexes, where diimine = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives (R_2bpy and R_2phen) and dithiolate = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (ecda), that are luminescent in solution and possess a long-lived charge-transfer excited state assigned as $^3(\mathrm{Pt(d)/S(p)} - \pi^*_{\mathrm{diimine}})$ with an approximate energy of 50 kcal/mol for the series.[24–28] In these complexes, the emission maxima occur in the range 550–600 nm. Cyclic voltammograms of these Pt(diimine)(dithiolate) complexes exhibit two reversible reduction waves in the ranges of −1.11 to −1.29 V and −1.68 to −1.83 V vs SCE and an irreversible oxidation wave.[25] Selected members of the series were shown to undergo electron-transfer quenching at near diffusion-controlled rates with the reductive quencher *N*,*N*-dimethylaniline and the oxidative quencher *o*-nitrobenzaldehyde.[24] These complexes were found to be stable to reductive quenching but to decompose during oxidative quenching. This behavior was totally consistent with the observed electrochemistry described above.

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(1) Adamson, A. W. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 10.
(2) Kalyanasundaram, K. In *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992.
(3) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.
(4) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909.
(5) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 241.
(6) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.
(7) Nagle, J. K.; Dressick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993.
(8) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081.
(9) Deronzier, A.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 2912.
(10) Miedlar, K.; Das, P. K. *J. Am. Chem. Soc.* **1982**, *104*, 7462.
(11) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.
(12) Fasano, R.; Hoggard, P. E. *Inorg. Chem.* **1983**, *22*, 566.
(13) Venturi, M.; Mulazzani, Q. G.; Ciano, M.; Hoffman, M. Z. *Inorg. Chem.* **1986**, *25*, 4493.
(14) Darwent, J. R.; Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 373.
(15) Creaser, I. I.; Gahan, L. R.; Geue, R. J.; Launikonis, A.; Lay, P. A.; Lydon, J. D.; McCarthy, M. G.; Mau, A. W.-H.; Sargeson, A. M.; Sasse, W. H. F. *Inorg. Chem.* **1985**, *24*, 2671.
(16) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
(17) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.
(18) Rillema, D. P.; Nagle, J. K.; Barringer, L. F., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56.
(19) Mandal, K.; Pearson, T. D. L.; Krug, W. P.; Demas, J. N. *J. Am. Chem. Soc.* **1983**, *105*, 701.
(20) Gsponer, H.; Argüello, G. A.; Argüello, G. A.; Staricco, E. H. *Inorg. Chim. Acta* **1991**, *189*, 207.
(21) Lee, S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 1367.
(22) Gamache, R. E., Jr.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141.
(23) Wan, K.-T.; Che, C.-M.; Cho, K. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1077.
(24) Zuleta, J. A.; Chesta, C. A.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, *111*, 8916.
(25) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47.
(26) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1991**, *111*, 237.
(27) Zuleta, J. A.; Bevilacqua, J. M.; Rehm, J. M.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 1332.
(28) Zuleta, J. A.; Bevilacqua, J. M.; Proserpio, D. M.; Harvey, P. D.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 2396.

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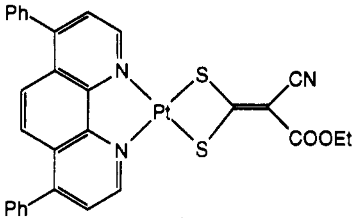
In order to determine experimentally the excited-state reduction potential of one of the complexes, we have undertaken a detailed quenching investigation on the complex Pt(Ph_2phen)(ecda), **1**, with



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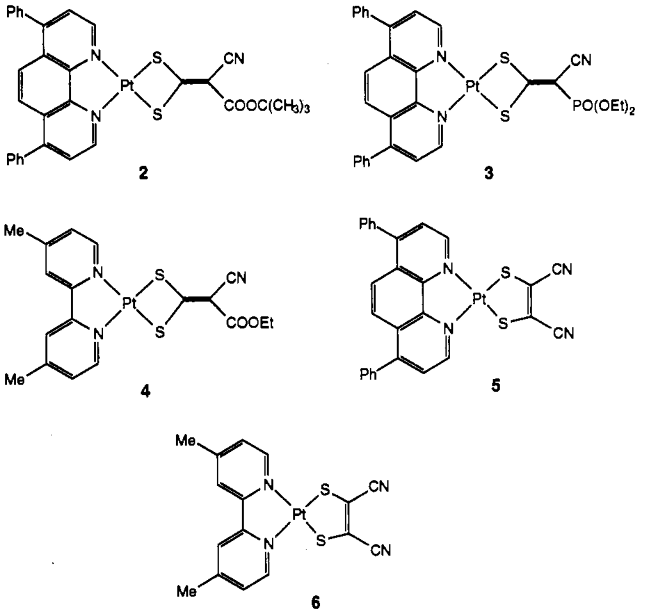
two types of reductive quenchers, aromatic amine donors and metallocene donors. The aromatic amine quenchers have a wide range of reversible and quasi-reversible reduction potentials, 0.12–1.21 V vs SCE.[3,29,30] The triplet energies of these quenchers (>62 kcal/mol)[31] are also higher than that estimated for Pt(Ph_2phen)(ecda) at 52 kcal/mol,[24] which means that energy transfer cannot compete with electron transfer in quenching of the Pt(Ph_2phen)(ecda) excited state by these amines. The metallocene quenchers were chosen for their similar size, stability, and wide range of reversible reduction potentials from –0.11 to 1.03 V vs SCE.[32] However, the low-lying d–d states of these quenchers fall between 38 and 46 kcal/mol above the ground state,[33-35] making them lower in energy than the triplet state of Pt(Ph_2phen)(ecda). The relative energies of these states thus permit energy transfer to compete with electron transfer in quenching of the Pt(Ph_2phen)(ecda) excited state. Competitive quenching of this type has been described previously by Lee and Wrighton, who found that ferrocenes undergo both electron-transfer and energy-transfer quenching with the excited state of $Ru(bpy)_3^{2+}$.[36]

Through the quenching studies described in the current paper, the excited-state reduction potential of Pt(Ph_2phen)(ecda) is determined experimentally and compared to an estimate obtained from a thermodynamic cycle based on the ground-state reduction potential and the zero–zero energy of the Pt(Ph_2phen)(ecda) excited state. This method of estimation is then extended to other Pt dithiolate systems that have been prepared in our laboratory shown in Chart 1. We also find that metallocenes, while effective quenchers of emission, do not function solely as electron-transfer quenchers with Pt(Ph_2phen)(ecda).

Experimental Section

Reagents. *N,N,N',N'*-tetramethyl-1,4-phenylenediamine, hexamethylbenzene, triphenylamine, and *N,N*-dimethylaniline (Aldrich) were purified by standard literature procedures.[37] Tris(4-tolyl)amine and tris-(4-bromophenyl)amine were generous gifts from Dr. Jerry Perlstein. The pure amines were handled under nitrogen. All metallocenes were commercially available except iodoferrocene which was prepared by a literature procedure.[38] Osmocene (Strem Chemical) was used as received without further purification. Decamethylferrocene (Strem Chemical), 1,1'-dimethylferrocene (Strem Chemical), ferrocene (Aldrich), and ruthenocene (Aldrich) were purified by three vacuum sublimations.

Chart 1



(Hydroxymethyl)ferrocene (Strem Chemical) was recrystallized twice from petroleum ether. The syntheses of Pt(Ph_2phen)(ecda) (**1**), Pt(Ph_2phen)(tbcda) (**2**), Pt(Me_2bpy)(ecda) (**4**), Pt(Ph_2phen)(mnt) (**5**), and Pt(Me_2bpy)(mnt) (**6**) have been described previously,[24-28] while Pt(Ph_2phen)(cpdt) (**3**) was prepared by a completely analogous method. Methylene chloride was dried over CaH_2 and vacuum transferred prior to use.

Spectroscopic Characterization. Infrared spectra were obtained from KBr pellets on a Mattson 6020 Galaxy Series FTIR spectrometer. Absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. Solution emission measurements were performed on deoxygenated samples using a Spex Fluorolog spectrophotometer using 380- and 456-nm excitation. Solution lifetimes were measured by single-photon counting (excitation wavelength of 380 nm); the instrumental setup has been described elsewhere.[25] The data were fit using the commercially available plotting program Sigma Plot version 4.1.

Kinetics. Quenching measurements were conducted at room temperature in methylene chloride. The complexes were sufficiently soluble and emissive in this solvent for reliable work. Steady-state fluorescence spectroscopy was the principal technique used for the kinetic determinations, although results of selected experiments were independently confirmed by lifetime measurements.

In a typical experiment, the deaerated sample solution was prepared in a 1-cm × 1-cm quartz fluorescence cell fitted with a needle-valve. The Pt(Ph_2phen)(ecda) concentration was maintained at $(1-3) \times 10^{-5}$ M in all samples and determined spectroscopically using the molar extinction coefficient of 12 430 M^{-1} cm^{-1} at 456 nm.[39] Quencher concentrations were between 0 and 1×10^{-2} M. The excitation wavelength for luminescence experiments was 456 and 380 nm and for lifetime experiments was 380 nm. The luminescence spectrum of each sample was measured, and the relative emission yields were determined as a function of quencher concentration. Intensities were recorded for at least five different concentrations of each quencher. Absorbances at 380, 456, and 600 nm were measured for each sample to correct for inner-filter effects.[40,41] Selected emission quenching experiments were followed by lifetime measurements. Specifically, the emission lifetime was monitored as a function of quencher concentration. For each experiment, the first measurement involved the emission lifetime without quencher present,

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(29) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498.

(30) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.

(31) Carmichael, I.; Hug, G. L. In *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press, Inc.: Boca Raton, Florida, 1989; Vol. 1, Chapter 16.

(32) Lemke, F. R.; Granger, R. M.; Morgenstern, D. A.; Kubiak, C. P. *J. Am. Chem. Soc.* **1990**, *112*, 4052.

(33) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(34) Wrighton, M. S.; Pdungsap, L.; Morse, D. L. *J. Phys. Chem.* **1975**, *79*, 66.

(35) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161.

(36) Lee, E. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8562.

(37) Perrin, D. D.; Perrin, D. R. In *Purification of Laboratory Compounds*; Pergamon Press Ltd.: New York, 1980.

(38) Fish, R. W.; Rosenblum, M. *J. Org. Chem.* **1965**, *30*, 1253.

(39) Bevilacqua, J. M.; Eisenberg, R. Unpublished results.

(40) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Chapter 9, pp 44–45. The luminescence intensity was corrected for inner filter effects by the equation

$$F_{corr} \cong F_{obs}\ \text{antilog}((OD_{ex} + OD_{em})/2)$$

where OD_{ex} and OD_{em} are the optical densities at the excitation and emission wavelength and F_{obs} is the observed fluorescence intensity at 600 nm. All samples had an absorbance less than 0.002 at the emission wavelength, 600 nm.

(41) The quenching rate was measured at both 456 and 380 nm to show that the luminescence experiments carried out with 456-nm excitation were comparable to the lifetime experiments obtained with 380-nm excitation.

Table 1. Rate Constants for the Quenching of *Pt(Ph_2phen)(ecda)[a] by Aromatic Amines in Methylene Chloride

no.	amine	$E(+/0)$, V vs SCE	k_q, 10^9 M^{-1} s^{-1} [b]	k_q', 10^9 M^{-1} s^{-1} [c]
1	$Me_2NC_6H_4NMe_2$	0.12	15.0	63.8
2	*p*-tritolylamine	0.75	4.4	5.7
3	*N*,*N*-dimethylaniline	0.81	5.8	8.2
4	N(*p*-C_6H_4Br)$_3$	1.05	0.73	0.76
5	triphenylamine	1.06	0.10	0.10
6	hexamethylbenzene	1.21	$<10^5$	$<10^5$

[a] [Pt(Ph_2phen)(ecda)] = (1–3) × 10^{-5} M. [b] k_q was calculated from the slope using τ_0(Pt(Ph_2phen)(ecda)*) = 20.9 ns. [c] Chemically activated rate constants calculated from eqs 4 and 5 in refs 3 and 42.

Table 2. Rate Constants for the Quenching of *Pt(Ph_2phen)(ecda)[a] by Metallocenes in Methylene Chloride

no.	metallocene	$E(+/0)$, V vs SCE	k_q, 10^9 M^{-1} s^{-1} [b]	k_q', 10^9 M^{-1} s^{-1} [c]
1	Fe(C_5Me_5)$_2$	–0.11	14.6	56.3
2	Fe(C_5H_4Me)$_2$	0.31	13.1	38.8
3	Fe(Cp)(C_5CH_2OH)	0.38	10.7	23.4
4	Fe(Cp)$_2$	0.48	10.6	22.7
5	Fe(Cp)(C_5H_4I)	0.54	10.2	20.9
6	Os(Cp)$_2$	0.83	7.3	11.5
7	Ru(Cp)$_2$	1.03	2.6	2.9

[a] [Pt(Ph_2phen)(ecda)] = (1–3) × 10^{-5} M. [b] k_q was calculated from the slope using τ_0(Pt(Ph_2phen)(ecda)*) = 20.9 ns. [c] Chemically activated rate constants calculated from eqs 4 and 5 in refs 3 and 42.

t_0. A value of 20.9 ± 1 ns was recorded in all experiments and was subsequently used to determine the quenching rate constant, k_q, from the slopes of the Stern–Volmer plots.

Results

The fluorescence intensity and emission lifetime of the excited state of Pt(Ph_2phen)(ecda) decreased as the concentration of quencher increased for all quenchers studied. Quenching constants (k_q) were measured by monitoring the decrease in luminescence intensity or emission lifetime as a function of quencher concentration. The fluorescence intensity data and emission lifetime data were plotted versus quencher concentration according to eq 1. In this equation, k_q is the experimental

$$F_0/F = \tau_0/\tau = 1 + k_q\tau_0[\mathrm{Q}] \qquad (1)$$

quenching rate constant, F_0 is the intensity of light emitted at a fixed wavelength in the absence of quencher, F is the emitted intensity in solutions with added quencher, τ_0 is the excited-state fluorescence lifetime for *Pt(Ph_2phen)(ecda), τ is the observed lifetime in solutions with quencher present, and [Q] is the concentration of quencher in solution.[40]

Linear Stern–Volmer plots were observed for the amine quenchers, but for the metallocene quenchers the Stern–Volmer plots differed depending on whether they were based on fluorescence intensity, in which case they were nonlinear, or emission lifetimes, where they were linear. The nonlinearity was attributed to inner-filter effects from the ferrocene derivatives, all of which absorb in the visible region. For the ferrocene quenchers, the fluorescence intensity plots corrected for inner-filter effects were linear over the range of quencher concentrations and the intercepts were unity as expected.[40] The values for k_q were determined from the slopes of the Stern–Volmer plots (the Stern–Volmer constants K_{SV}) and the measured value of τ_0 = 20.9 ns for the emission lifetime of *Pt(Ph_2phen)(ecda) in solutions containing no quencher. Absorbance-corrected quenching rate constants k_q are shown for the amine and metallocene quenchers in Tables 1 and 2, respectively. Also, for selected experiments lifetime measurements were carried out. Plots of τ_0/τ vs [Q] were linear for all quenchers and gave results in good agreement with the fluorescence quenching. The k_q' values in Tables 1 and 2 are k_q values that have been corrected for diffusional effects.[3,42–44]

Correction for diffusional effects is important for the most rapid quenching rate constants because the rate constants become diffusion limited. The corrected k_q' values are the quenching rate constants assuming that the excited-state chromophore and quencher are in contact at the moment of excitation.

Following an analysis based on Marcus theory similar to that given by Bock *et al.*,[3] the bimolecular rate constants k_q' for electron-transfer quenching relate to the free-energy change of the electron transfer process, ΔG_{et}, through eq 2,where $k_q'(0)$ is

$$RT\ln k_q' = RT\ln k_q'(0) - \frac{\Delta G_{et}}{2}\left(1 + \frac{\Delta G_{et}}{2\lambda}\right) \qquad (2)$$

the chemically activated electron-transfer rate constant when ΔG_{et} = 0 for a series of similar quenchers and λ is the complex and solvent sphere reorganization energy which determines the activation barrier for electron transfer.[45–52] The free energy change of electron transfer, ΔG_{et}, depends on the excited-state reduction potential of Pt(Ph_2phen)(ecda) denoted $E(\mathrm{Pt}^{*/-})$, the oxidation potential of the amine or metallocene quencher (*i.e.*, the reduction potential for the amine(+/0) or ferrocene(+/0) couple), and the work terms, W_r and W_p, required to bring reactants and products together, respectively, as given by eq 3.

$$\Delta G_{et}(\mathrm{V}) = [E(\mathrm{Pt}^{*/-}) - E(\mathrm{Ox/Red})] + W_p - W_r \qquad (3)$$

For the amine quenchers, a plot of $RT \ln k_q'$ vs $E_{1/2}$ of the amine(+/0) shows a region of linear increase with decreasing $E_{1/2}$ and a diffusion-limited plateau at low $E_{1/2}$ where the amine is easier to oxidize (Figure 1). The slope of the linear increase is *ca.* 0.5, which is in accord with expectation.[3] The corresponding plot for quenching by metallocenes shows a much decreased dependence of quenching rate on $E_{1/2}$ as would be anticipated for a series of quenchers which function by energy transfer as well as by electron transfer. From Figure 1, it is possible to estimate the electron-transfer rate for ΔG_{et} = 0, $k_q'(0)$, which in turn allows determination of the excited-state reduction potential. An alternative approach followed by Meyer and Whitten[3] for estimating $k_q'(0)$ based on the Marcus cross-relation is not feasible in the present study since we have no measure of the excited-state

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(42) Corrections for diffusional effects using eq 4 are necessary because for most of the quenching reactions the rate constants approach the diffusion-controlled limit. In eq 4, k_q is the measured quenching rate constant, k_q' is the rate constant for activated quenching, and k_d is the diffusion-limited rate constant in methylene chloride, which is determined by eq 5,

$$1/k_q = 1/k_q' + 1/k_d \qquad (4)$$

$$k_d = \frac{2RT}{3\eta}\left(2 + \frac{r_A}{r_B} + \frac{r_B}{r_A}\right) \qquad (5)$$

where r_A and r_B are the average radius of Pt(Pt_2phen)(ecda) and the quenchers (r_{Pt} = 8.0 Å, r_{Am} = 3.6 Å, r_{Mc} = 4.1 Å) and η is the solvent viscosity (3.9 × 10^{-4} kg m^{-1} s^{-1} for CH_2Cl_2). The k_q' values in Tables 1 and 2 were calculated using k_d = 1.9 × 10^{10} M^{-1} s^{-1} for the neutral amine quenchers and k_d = 2.0 × 10^{10} M^{-1} s^{-1} for the metallocene quenchers.

(43) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.

(44) von Smoluchowski, M. *Z. Phys. Chem.* **1917**, *92*, 129.

(45) On the basis of the theory of Marcus and Hush, ΔG_{et} can be calculated from reduction values for the redox couples involved if the electrostatic energies associated with bringing together the reactants (W_r; Pt* + Q) and products (W_p; Pt^- + Q^+) are taken into account according to eq 3. The electrostatic energies can be calculated using the equation

$$W(\mathrm{kcal/mol}) = (9.10 Z_A Z_B/d)[1/(1 + 0.48 d\sqrt{\mu})]$$

in which Z_A and Z_B are the ion charges, μ is the ionic strength, and d is the distance (in Å) between the ion centers. The work to bring the reactants (Pt* + Q) together in eq 3 (W_r) was assumed to be negligible because both species are uncharged. The work to separate products (Pt^- + Q^+) in eq 3 (W_p) was calculated to have an upper limit of 0.039 eV by assuming that the solution ionic strength is negligible.

(46) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

(47) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(48) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(49) Hush, N. S. *Chem. Phys.* **1975**, *10*, 361.

(50) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(51) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(52) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213 and references therein.

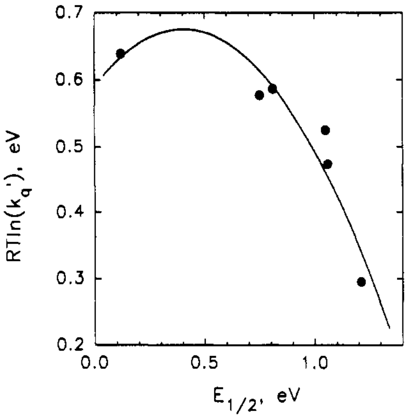
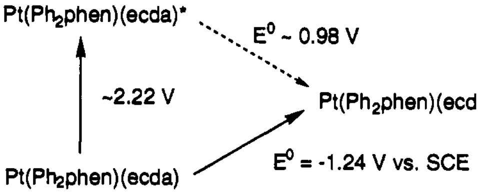


Figure 1. Plot of $RT\ln(k_q')$, V, versus $E_{1/2}$, V, at 25 °C for the quenching of *Pt(Ph_2phen)(ecda) by neutral amine donors. The solid circles represent the experimental data, and the solid line is the least-squares fit to eqs 2 and 3, where $E(\mathrm{Pt}^{*/-})$, $RT\ln(k_q'(0))$, and λ are calculated to be 0.93, 0.55, and 0.48 V, respectively.

Scheme 1



self-exchange rate constant for Pt(Ph_2phen)(ecda). However, values obtained from subsequent least-squares fitting of Figure 1 suggest that the excited-state self-exchange rate constant for *Pt(Ph_2phen)(ecda) is similar in magnitude to that of *Ru(bpy)$_3^{2+/+}$. The data for the amine quenchers is fit well by eqs 2 and 3 as shown by the solid line and leads to the estimate of the excited-state reduction potential of Pt(Ph_2phen)(ecda) as 0.93 V. The least-squares fit of the plot also yields a value of the reorganization energy λ of 0.485 V.

For the metallocene quenchers, one can estimate the rate constants for electron-transfer quenching using Marcus theory and the electron-transfer rate constants obtained with the amine quenchers. With these estimates it is then possible to calculate the rate of electron-transfer and energy-transfer quenching that the metallocene do with *Pt(Ph_2phen)(ecda).

Discussion

For the title complex, Pt(Ph_2phen)(ecda), it is possible to construct a simple thermodynamic cycle that allows an estimate to be made of the excited-state reduction potential. This cycle is shown in Scheme 1 and relies on the reversible reduction potential for Pt(Ph_2phen)(ecda) and the excited-state energy E_{00} defined as the energy difference between the zero vibrational levels of the ground and excited states. In practice, E_{00} is estimated spectroscopically from the crossing point of the emission and excitation spectrum and in the present case has a value of ~2.22 V (~52 kcal/mol).[23] The reversible reduction potential of Pt(Ph_2phen)(ecda) determined by cyclic voltammetry is −1.24 V vs. SCE. Thus according to Scheme 1, the excited-state reduction potential of Pt(Ph_2phen)(ecda), $E(\mathrm{Pt}^{*/-})$, is estimated at 0.98 V vs SCE.

The minimal reaction sequence that describes the quenching kinetics is presented in Scheme 2, where Pt designates the complex Pt(Ph_2phen)(ecda) and Q represents either the neutral amine or metallocene quencher. Following the absorption of light, excited *Pt forms an encounter complex with quencher denoted *Pt··Q via diffusion. The encounter complex can either dissociate or undergo electron transfer or energy transfer depending upon the nature of the quencher. In Scheme 2, both electron-transfer and energy-transfer pathways are shown with k_q(et) being the rate constants for electron transfer and k_q(en) the rate constant for energy transfer. While cage escape of the electron-transfer product $\mathrm{Pt}^- + \mathrm{Q}^+$ is in principle possible with a rate constant of k_{es}, the low dielectric constant of CH_2Cl_2 and the attraction between the oppositely charged ions makes it unlikely.[22] Thus, both electron-transfer and energy-transfer products are assumed to convert rapidly and irreversibly by back-electron-transfer and nonradiative decay, respectively, into the reactant molecules in their ground electronic states, Pt + Q.

Scheme 2

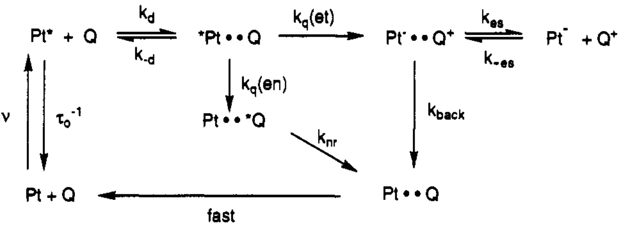


Table 1 lists the quenching rate data for the amine quenchers. The quenching rate decreases sharply as the amine becomes more difficult to oxidize corresponding to an increase in $E_{1/2}$ for the amine(+/0) couple. For example, k_q for *N,N,N',N'*-tetramethyl-1,4-phenylenediamine ($E_{1/2}$ = 0.12 V) is 19.0 × 10^9 M^{-1} s^{-1}, while k_q for hexamethylbenzene ($E_{1/2}$ = 1.21 V) is less than 10^5 M^{-1} s^{-1}. Energy transfer from *Pt(Ph_2phen)(ecda) to the neutral amine donors is unfavorable with these quenchers due to their relatively high triplet energies. The pronounced falloff in the k_q value as $E_{1/2}$ becomes positive is expected for electron-transfer quenching only and affirms the correctness of this assumption. The analysis of the data in Table 1 in terms of eqs 2 and 3 is thus relatively straightforward and leads to the excited-state reduction potential, $E(\mathrm{Pt}^{*/-})$, of 0.93 V, which agrees with the value of 0.98 V estimated via Scheme 1.

The variables in eq 2, $RT\ln k_q'(0)$ and λ, fit the data best when set to 0.55 and 0.48 V, respectively. These values are similar to those of 0.52 and 0.48 V determined by for the excited-state reduction potential of Ru(bpy)$_3^{2+}$.[3] The study of Ru(bpy)$_3^{2+}$ by Bock *et al.* serves as a model for the present study of Pt(Ph_2phen)(ecda) because both investigations use the same amines for reductive quenching. There exists only a small difference in the chemically activated electron-transfer rate constant, $k_q'(0)$, for amine quenching of the excited states of the two complexes, suggesting that Pt(Ph_2phen)(ecda) possesses a self-exchange rate for the excited state/anion couple which is similar to that estimated for Ru(bpy)$_3^{2+}$. It should be noted, however, that the amine quenching studies for Ru(bpy)$_3^{2+}$ and Pt(Ph_2phen)(ecda) were performed in different solvents, acetonitrile for the former and methylene chloride in the present study. The relative emission quantum yield[53] and the solution lifetime of Pt(Ph_2phen)(ecda)[24-28] are roughly 2-fold lower in acetonitrile compared with methylene chloride. The value of λ is more difficult to predict because it is dependent on both the internal and solvent reorganization energies prior to electron transfer. While the solvent reorganization component should be low because methylene chloride is relatively nonpolar and noncoordinating, the internal reorganization energy of Pt(Ph_2phen)(ecda) may be high because substantial charge redistribution may exist in the reduced platinum complex from its excited state.

All of the metallocenes are effective quenchers of the excited state. Table 2 lists the bimolecular quenching rates and the reduction potentials of the metallocenes studied. In contrast to the amine quenchers, the quenching rate constants, k_q, decrease only slightly as the metallocene becomes more difficult to oxidize. For example, the quenching rate constants for bis(pentamethyl)-

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(53) The relative emission quantum yield of Pt(Ph_2phen)(ecda) (0.0048 in methylene chloride) was determined by using Ru(bpy)$_3^{2+}$ in DMF (0.068 in DMF) as a standard (7.1% of Ru(bpy)$_3^{2+}$): Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1639.

Scheme 3

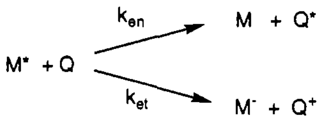

Table 3. Determination of the Rate of Electron- and Energy-Transfer Quenching of *Pt(Ph_2phen)(ecda) by Metallocene Quenchers

metallocene no.	$\Delta E°$, V[a]	K_{12}[b]	f_{12}[c]	k_{el}, $M^{-1}\ s^{-1}$[d]	k_{en}, $M^{-1}\ s^{-1}$[e]
1	1.04	3.82×10^{17}	8.3×10^{-23}	1.1×10^{6}	5.6×10^{10}
2	0.72	1.49×10^{12}	2.6×10^{-11}	1.3×10^{9}	3.7×10^{10}
3	0.55	1.99×10^{9}	6.7×10^{-7}	7.4×10^{9}	1.6×10^{10}
4	0.45	4.05×10^{7}	7.3×10^{-5}	1.1×10^{10}	1.2×10^{10}
5	0.39	3.92×10^{6}	7.8×10^{-4}	1.1×10^{10}	9.9×10^{9}

[a] $\Delta E°$ of the reaction $Pt^* + Mc \rightarrow Pt^- + Mc^+$ is estimated using $E(Pt^*/-)$ determined from the amine quenching studies and the measured reversible reduction potential for the metallocene(+/0) couple. [b] $K_{12} = 10^{(\Delta E°/0.05915)}$. [c] $\log f_{12} = (\log K_{12})^2/[4 \log(k_{11}k_{22}/Z^2)]$, where k_{11} of $3.4 \times 10^9\ M^{-1}\ s^{-1}$ corresponds to the self-exchange rate of Pt(Ph_2phen)(ecda)*/Pt(Ph_2phen)(ecda)⁻ determined using the aromatic amine quenchers, $k_{22} = 1.2 \times 10^7\ M^{-1}\ s^{-1}$ from ref 55, and the collision frequency $Z = 1 \times 10^{10}\ M^{-1}\ s^{-1}$. [d] $k_{et} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$. [e] $k_q' = k_{et} + k_{en}$.

ferrocene and ruthenocene decrease from 14.6×10^9 to 2.6×10^9 $M^{-1}\ s^{-1}$ as the quencher reduction potential increases from –0.11 to 1.03 V. Since the falloff in the k_q value (Table 2) is not very pronounced as ΔG_{et} becomes more positive, the quenching results cannot be explained by electron transfer alone. Competitive electron-transfer and energy-transfer quenching of metal complex excited states by metallocenes has been noted previously and arises because of the low energy triplet excited states that the metallocenes possess, ranging from 38 to 46 kcal/mol above the ground state.[36] The metallocene quenching behavior can thus be represented by a combination of electron- and energy-transfer quenching according to Scheme 3. In this scheme, the overall quenching rate constant corrected for diffusional effects, k_q', is the sume of k_{et} and k_{en}. Partitioning of k_q' into k_{et} and k_{en} is possible on the basis of the results obtained with the amine quenchers, leading to calculated rates of electron-transfer and energy-transfer quenching for each of the metallocenes in Table 3.

Previously, McMillin *et al.*[53] were able to deconvolute the values of k_{et} and k_{en} from k_q for the excited-state quenching of $Cu(Ph_2phen)_2^+$ by a series of $Cr(acac)_3$ derivatives, assuming an average energy-transfer rate, k_{en}. While this may be a valid assumption for the $Cr(acac)_3$ systems because the low-lying d–d states of these compounds are virtually isoenergetic,[54] it is not a good assumption for the metallocene quenchers. Lee and Wrighton have shown that the partitioning of quenching between electron and energy transfer varies widely in the metallocene quenchers, indicating that an average k_{en} would not be a good approximation.[36] In their study of the quenching of $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpz)_3^{2+}$ (where bpy = 2,2′-bipyridine and bpz = 2,2′-bipyrazine) by ferrocene and its methylated derivatives, Lee and Wrighton showed that quenching occurs competitively by both electron and energy transfer with the electron transfer component of quenching increasing as the driving force for electron transfer increases.[36] The present results are totally consistent with that deconvolution of electron- and energy-transfer rates from the total quenching rate constant.

Related Pt(diimine)(dithiolate) Systems. Since agreement between the excited-state reduction potential obtained by the thermodynamic cycle of Scheme 1 and that obtained from the quenching studies is rather good, we have employed the former to estimate the excited-state reduction potentials of a number of related Pt(diimine)(dithiolate) complexes, illustrated in Chart 1. These complexes have similar electronic and excited-state properties.[24–28] The excited-state reduction potentials $E(Pt^{*/-})$ along with the ground-state reduction potentials and E_{00} values are presented in Table 4. The E_{00} values are determined from the crossing point of the highest energy emission maximum and the lowest energy excitation maximum of each complex.

Table 4. Estimated Excited-State Reduction Potentials of Related Pt(diimine)(dithiolate) Complexes

complex	$E(0/-)$, V vs SCE	E_{00}, eV[a]	$E(Pt^*/-)$, V vs SCE
Pt(Ph_2phen)(ecda) (**1**)	–1.24	2.22	0.98
Pt(Ph_2phen)(tbcda) (**2**)	–1.22	2.21	0.99
Pt(Ph_2phen)(cpdt) (**3**)	–1.21	2.21	1.00
Pt(Me_2bpy)(ecda) (**4**)	–1.21	2.36	1.15
Pt(Ph_2phen)(mnt) (**5**)	–1.09	2.14	1.04
Pt(Me_2bpy)(mnt) (**6**)	–1.17	2.13	0.96

[a] Determined from the crossing point of the emission and excitation spectra.

The excited-state reduction potentials $E(Pt^{*/-})$ of ~1.0 V (vs SCE) estimated here for **1**–**6** are similar in energy to the those of $Ru(bpy)_3^{2+}$ derivatives which have excited-state reduction potentials, $E(Ru^{2+*/+})$, between 0.8 and 1.4 V (vs SCE). We therefore expect that the Pt(diimine)(dithiolate) systems will prove to be good photocatalysts. However, some drawbacks exist in the Pt diimine complexes containing 1,1-dithiolates (ecda, tbcda, cpdt) including diminished emission quantum yields and short lifetimes (<10 ns) in polar organic solvents. The complexes containing the 1,2-dithiolate mnt also suffer from low solubility in all organic solvents. Studies are continuing on systems which we expect will not suffer from these drawbacks while maintaining the attractive electronic structural features of the Pt(diimine)(dithiolate) complexes including their coordinative unsaturation.

Conclusions

The charge-transfer excited state of Pt(Ph_2phen)(ecda) is a strong oxidant which undergoes facile electron transfer, as has been shown by quenching studies with series of neutral amine and metallocene donors. The quenching rate results for the metallocene series are more complicated because competitive energy-transfer and electron-transfer quenching occur and the two rates partition differently for each metallocene. The quenching results for the amine donors are consistent with electron-transfer quenching exculsively. The results have been analyzed in order to obtain the excited-state reduction potential. The value $E(Pt^{*/-})$ determined by a Marcus analysis is 0.93 V vs SCE, which is close to the value of 0.98 V vs SCE estimated from a thermodynamic cycle based on the reversible reduction potential $E_{1/2}$ and the E_{00} energy of the excited state. The excited-state reduction potential has been estimated for a number of related Pt(diimine)(dithiolate) complexes that have electronic and excited-state properties similar to those of Pt(Ph_2phen)(ecda) (**1**). The related complexes, Pt(Ph_2phen)(tbcda) (**2**), Pt(Ph_2phen)(cpdt) (**3**), Pt(Me_2bpy)(ecda) (**4**), Pt(Ph_2phen)(mnt) (**5**), and Pt(Me_2bpy)(mnt) (**6**), all have excited-state reduction potentials close to 1.0 V versus SCE. These values are similar to those of the extensively studied d^6 $Ru(diimine)_3^{2+}$ systems.

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(54) Lintvedt, R. L.; Fenton, D. E. *Inorg. Chem.* **1980**, *19*, 569.

(55) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.