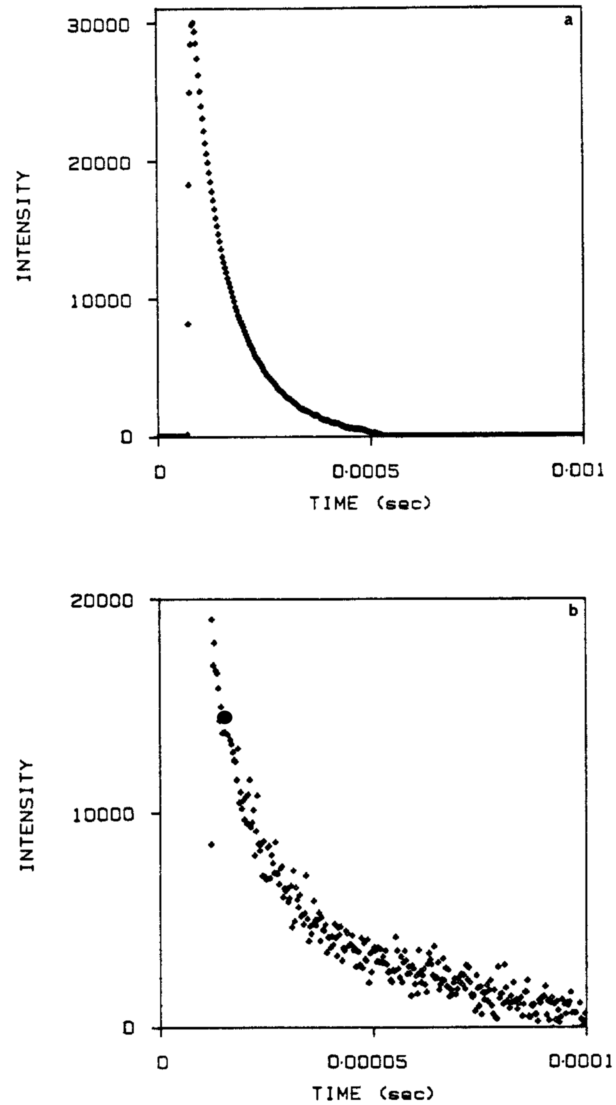

Figure 1. Time-resolved decay of the emission intensity for (a) $a_5Ru^{3+}(48)MbPd^*$ and (b) $a_4pyRu^{3+}(48)MbPd^*$ monitored at 670 nm following 532 nm pulsed laser excitation. The observed decay rates (k_D) are 1.0 (5) × 10^4 and 9.1 (5) × 10^4 s^{-1}, respectively. Conditions: 25 °C, 0.01 M pH 7 phosphate, O.D. (390 nm) = 0.5–1.0.

limits we place on the reorganization energy in Ru(48)MbM.[14] The relatively large λ (1.90–2.45 eV) is similar to those reported for ET in Ru(33)cyclochrome c[Zn][11] and in hemoglobin [Zn,-Fe].[15] The high reorganization energy in these protein systems probably can be attributed to reorganization of the aqueous medium around the redox sites. The faster ET rates observed for rigid aliphatic systems[16] may be due to the low $\lambda(\sim 1$ eV) in nonaqueous media and not an enhanced donor–acceptor electronic coupling. In fact, the β of 0.91 $Å^{-1}$ determined for Mb[12] is nearly the same as the 0.85 $Å^{-1}$ decay factor reported[16b] for one of the organic donor–acceptor systems.

Our work indicates that very high ET rates in proteins could be realized at relatively small driving forces if λ were reduced to

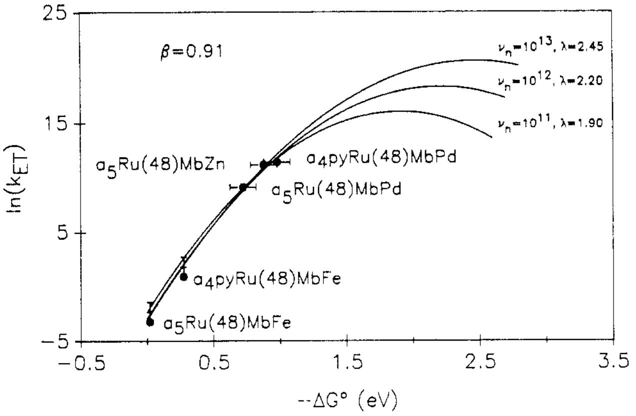

Figure 2. Free energy dependence of ln k_{ET}. The ln k_{ET} (Fe) error bars correspond to a 1 (1) Å uncertainty in the ET distance; this uncertainty arises because of differences in the delocalization of the MP ET orbital (Fe is more localized than Zn or Pd).

1 eV or less. (At a driving force of 0.1 V with λ = 1 eV and β = 0.9 $Å^{-1}$, for example, the rate calculated for 15 Å ET is 8 × 10^4 s^{-1}.) It would be surprising if biological systems did not use such reductions in reorganization energy to achieve specificity.

Acknowledgment. We thank Mike Albin for helpful discussions. This work was supported by National Science Foundation Grant CHE85-18793. C.M.L. acknowledges postdoctoral fellowship support from the NIH.

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[13] The curves in Figure 2 were calculated by using a Marcus expression[2] for the ET rate, $k = \nu_n \exp[-\beta(d - 3)] \exp[-(\Delta G° + \lambda)^2/4\lambda RT]$. The values of β (0.91 $Å^{-1}$) and d (13.2 Å) have been determined previously for RuMbZn.[12] The curves were fit to the experimental data by varying λ, with ν_n fixed at 10^{11}, 10^{12}, or 10^{13} s^{-1}.

[14] The finding that all five rates can be fit satisfactorily with a single λ indicates that outer-sphere contributions (λ_0) dominate, because λ_i is expected[6] to be larger for Fe than for Zn or Pd.

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Carbanion Intermediates in the Photodecarboxylation of Benzannelated Acetic Acids in Aqueous Solution

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Organic photochemical reactions proceeding via carbanion intermediates are not common. Several photodecarboxylations[1,2] and a photoretro-aldol type reaction[3] have been reported as proceeding via carbanions. On the other hand, the photochemistry of carbanions has been well-documented.[2a,4] Essentially nothing is known about the ability of cyclic hydrocarbon π-systems in stabilizing carbanions in the excited state, whereas Hückel's $4n + 2$ rule works well for the corresponding ground-state systems.[5] One method[6] to probe the relative stability of charged cyclic π-systems in the excited state is to study the reactivity of suitably designed molecules capable of producing such intermediates on photolysis. We have thus reported results which suggest that cyclic 4π-electron carbocations are better accommodated than cyclic 6π-electron carbocations in the excited state, via study of photosolvolysis of benzannelated alcohols.[7,8] We now report results which show that the photodecarboxylation of several benzannelated acetic acids proceed via carbanion intermediates and in addition,

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† NSERC University Research Fellow, 1984–1989.

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[8] Subsequent to publishing the paper, we have established that the observed difference in quantum yields between fluoren-9-ol and dibenzosuberenol (5*H*-dibenzo[*a,d*]cyclohepten-5-ol) is not due to a difference in lifetimes, since fluoren-9-ol (the more reactive compound) is significantly shorter lived (τ < 0.1 ns) than dibenzosuberenol (τ = 0.84 ns) in aqueous solution.

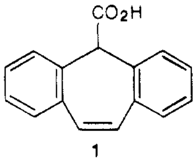
Table I

compd	% yield[a]	(Φ/Φ°)[b]	compd	% yield[a]	(Φ/Φ°)[b]
1	50	1.0	4	12	0.24
2	≤ 3	≤ 0.06	5	16	0.32
3	7	0.14	6	6	0.12

[a] Yield of photodecarboxylation product calculated by ^1H NMR integration. Solutions (10^{-3} M) were photolyzed in quartz vessels under argon at 254 nm in a Rayonet RPR 100 photochemical reactor. Typical photolysis time was 5 min with use of eight lamps. The pH of the solution (20% CH_3CN) was adjusted with aqueous NaOH and monitored by a pH meter. Errors are ±10% of quoted value. [b] Relative quantum yield of photodecarboxylation using the yield of compound **1** as the reference.

that eight-electron ($4n$) carbanions (in a conjugated cyclic π-system) are better accommodated than six-electron ($4n + 2$) carbanions in the excited singlet state. We also report that ESR spectrometry can provide a useful method for the detection of photogenerated carbanions.

The photodecarboxylations of several benzannelated acetic acids **1**–**5** were studied, with diphenylacetic acid (**6**) as the noncyclic model compound. In the ground state, fluorene-9-carboxylic acid (**2**) decarboxylates cleanly to give fluorene (**7**) in aqueous solution at pH > pK_a (≈ 4) at 80 °C, with a half-life of about 10 h. Under these conditions, **1** (5*H*-dibenzo[*a*,*d*]cyclohepten-5-carboxylic acid) and **3**–**6** failed to react. A similar observation has been noted in a previous study of the decarboxylation of these and related compounds.[9] When **2** is thermally decarboxylated in D_2O, deuterium is incorporated at the 9-position of product **7** and indicates that a carbanion intermediate is involved in the thermal reaction. Additionally, Hückel's $4n + 2$ rule applies here in predicting which system would be reactive as **2** is the only one which can give a very stable carbanion intermediate.



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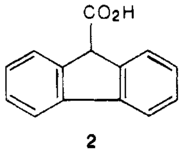
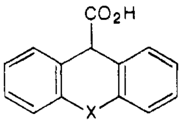
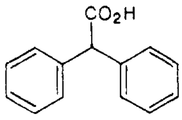


2



3, X = CH_2CH_2
4, X = O
5, X = S



6

On photolysis at 254 nm in aqueous solution, all of **1**–**6** photodecarboxylate cleanly, to give the corresponding hydrocarbons for **1**–**3** and **6** and to xanthene[10] and thioxanthene for **4** and **5**, respectively. However, there are striking differences in the observed relative quantum yields for photoreaction (Table I). The most striking feature is that **1** has the highest quantum yield of photodecarboxylation. Measurements using photodecarboxylations of *p*-nitrophenyl acetate[1a] ($\Phi \approx 0.6$) and 3-pyridylacetic acid[11] ($\Phi = 0.45$) as secondary actinometers gave $\Phi \approx 1 \pm 0.1$ for reaction of **1**. Thus the relative quantum yields (Φ/Φ°) of Table I may be taken as a good approximation to their respective absolute quantum yields of reaction. To our knowledge, compound **1** has the highest quantum yield of photodecarboxylation of any organic compound, whereas it is inert to decarboxylation in the ground state! In contrast, fluorene-9-carboxylic acid (**2**) has the lowest quantum yield of photodecarboxylation, even lower than **3** and **6**, which do not have a conjugated internal cyclic array. Evidence which suggests that these photodecarboxylations are via the singlet excited state is the observation that **1** is weakly fluorescent ($\Phi_f < 0.01$) and **3** strongly fluorescent ($\Phi_f \geq 0.4$) in aqueous solution, whereas in pure CH_3CN—where both **1** and **2** are nonreactive—their fluorescence efficiencies are similar to the corresponding hydrocarbons fluorene (**7**) and dibenzosuberene (**8**)

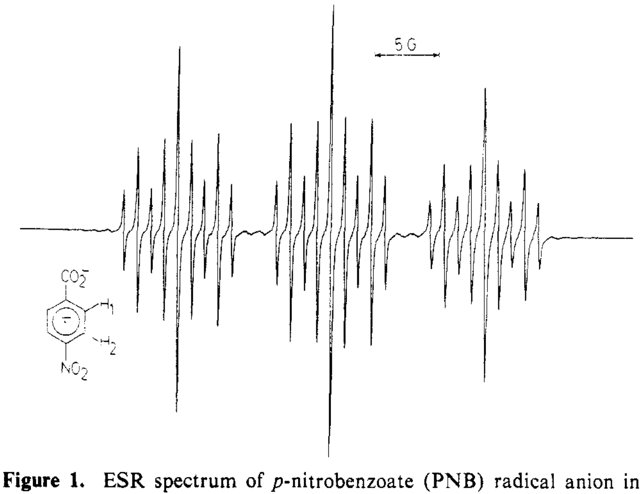
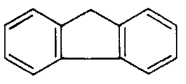


Figure 1. ESR spectrum of *p*-nitrobenzoate (PNB) radical anion in aqueous solution observed on photolysis of **1** (10^{-3} M) with PNB (10^{-2} M) in aqueous solution at pH 12. Coupling constants (via computer simulation of spectrum) are $a_N = 13.15$ G, $a_{H1} = 1.15$ G, and $a_{H2} = 3.45$ G.



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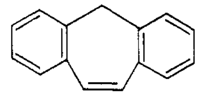

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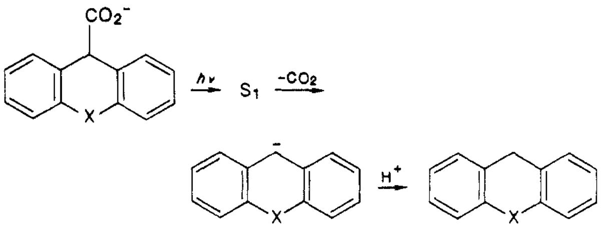
both of which are known to be highly fluorescent, with $\Phi_f > 0.2$.[12,13] Additionally, triplet sensitization of reaction of **1** ($E_T \leq 60$ kcal mol^{-1})[12] with sodium benzophenone-2-carboxylate ($E_T \approx 68$ kcal mol^{-1})[12] failed to give any reaction.

Single-photon counting fluorescence lifetime measurements in aqueous solution show that **2** has a lifetime of 4.7 ± 0.05 ns while that of **1** = 0.13 ± 0.05 ns, which indicates that the observed quantum yield difference between **1** and **2** is only a lower limit of the difference in intrinsic reactivity of the two systems.

The observations of deuterium incorporation in the isolated photodecarboxylation products of **1**–**6** when photolyses are carried out in D_2O and that **2**–**6** are photochemically nonreactive at pH < pK_a argue for a mechanism involving heterolytic cleavage of the carboxylate anion to give a carbanion intermediate in the primary photochemical step (eq 1).[14] However, **1** reacts efficiently even at pH < pK_a which indicates an extremely reactive chromophore, unlike those of **2**–**6**, which require the carboxylate anion form to facilitate the departure of the carbanion.



(1)

When aqueous solutions of **1**–**6** are photolyzed in a quartz flat-cell with added *p*-nitrobenzoic acid at pH ≥ 7 inside the cavity of a Bruker E200TT ESR spectrometer, very weak to intense ESR signals assignable to the radical anion of *p*-nitrobenzoate (PNB)

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(9) Toussaint, O.; Capdeville, P.; Maumy, M. *Tetrahedron* **1984**, *40*, 3229.

(10) The xanthene product from **4** undergoes additional *secondary* photochemistry in aqueous solution, to give 9,9′-bisxanthene.

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(13) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978. Dibenzosuberene (**8**) is much more rigid than *cis*-stilbene and hence has significant fluorescence emission in fluid solution.

(14) A photodecarboxylation mechanism of carboxylate anions involving initial photoejection of an electron has been proposed[2] and ruled out for the present reactions since no radical coupling products are observed. The observation of deuterium incorporation from D_2O is also convincing evidence for the proposed mechanism (eq 1).

are observed (Figure 1). The spectrum agrees well with those reported in the literature for PNB radical anion.[15] The strongest signals are observed for **1**, **4**, and **5** (which have significant quantum yields of photodecarboxylation); the same signals are also observable for **2**, **3**, and **6**. Photolysis of phenylacetate anion ($\Phi \approx 0.01$)[1,16] with PNB gave only very weak ESR signals. Photolysis of PNB alone or **1–6** in the absence of PNB does not give any ESR signal. It seems clear that **1–6** are sources of electrons on photolysis. We have ruled out a simple electron photoejection mechanism from the photoexcited carboxylate anions since carboxylate anions such as sodium benzoate—which do not photodecarboxylate—failed to give any ESR signal on photolysis with PNB. That the photogenerated carbanions are the sources of electrons is therefore implicated.

In summary, the results suggest that a simple "electron-count" rule applies for predicting the relative reaction efficiencies when dealing with photochemical reactions capable of generating charged conjugated cyclic arrays as intermediates. In the excited singlet state, a $4n$-electron count is favored over the usual $4n + 2$ system commonly observed in the ground state.[17,18]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for an operating grant, a post-graduate scholarship to E.K., and a summer research award to I.M. Single-photon fluorescence lifetime measurements and analyses were carried out at the Center for Fast Kineics Research at The University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Research Program of the Division of Research Resources of NIH (RR00886) and by The University of Texas at Austin. Additional support from the University of Victoria is also acknowledged.

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(16) Margerum, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 3772.

(17) For theoretical calculations of excited state annulenes, see: (a) Padma Malar, E. J.; Jug, K. *Tetrahedron* **1986**, *42*, 417. (b) Padma Malar, E. J.; Jug, K. *J. Phys. Chem.* **1984**, *88*, 3508. (c) Fratev, F.; Monev, V.; Janoschek, R. *Tetrahedron* **1982**, *38*, 2929.

(18) It should be noted here that the Woodward–Hoffmann[19] rules do not apply to the reactions studied in this work or to the photosolvolysis of fluoren-9-ol.[7]

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A Mixed-Valence Tetranuclear Platinum(I,II) Complex with a Pt(I)–Pt(I) Bond

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In the last two decades, dinuclear metal–metal bonded platinum(I) complexes have been the subject of numerous spectroscopic, structural, and electrochemical studies.[1] Almost all these diplatinum(I) compounds contain platinum–carbon bonds or ligands such as phosphines and hydrides and are prepared under anaerobic conditions in nonaqueous solvents.

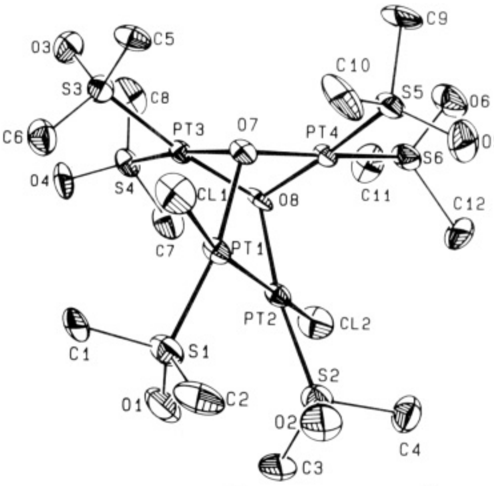
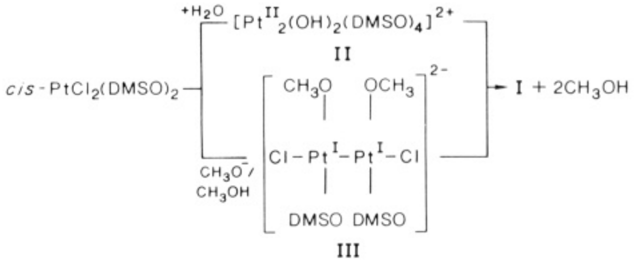


Figure 1. The structure of $[Cl_2Pt^I_2(DMSO)_2(\mu_3\text{-}O)_2Pt^{II}_2(DMSO)_4]$, I, as found in **2**: average Pt^I–Cl 2.470 (5), Pt^I–S 2.169 (5), Pt^I–O 2.06 (1), Pt^{II}–O 2.03 (1), Pt^{II}–S 2.221 (5) Å.

Scheme I



We report here the preparation and structural characterization of an unusual mixed-valence platinum(I,II) tetranuclear complex which contains a metal–metal bonded diplatinum(I) unit. Air stable compounds, containing the tetranuclear complex $[Cl_2Pt^I_2(DMSO)_2(\mu_3\text{-}O)_2Pt^{II}_2(DMSO)_4]$, I, are easily prepared in solutions containing water and in the open.[2] A detailed X-ray analysis of three different solvates, $[Pt_4Cl_2O_2(DMSO)_6]\cdot X$ ($X = 2H_2O$, **1**; $X = H_2O\cdot DMF$, **2**; $X = CH_2Cl_2$, **3**), showed that the structure and dimensions of I in **1–3** are almost identical.[3] The tetranuclear complex, depicted in Figure 1, consists of a dimeric $Pt^I_2Cl_2(DMSO)_2$ unit fused into a dimeric $Pt_2^{II}O_2(DMSO)_4$ unit by the formation of two μ_3-oxo bridges. Each oxygen atom bridges one Pt(I) and two Pt(II) atoms and the Pt_4O_2 unit can be described as a distorted cubane-type framework in which two oxygen atoms are missing. The O–Pt^I–Pt^I–O system deviates significantly from planarity with torsional angles of about 28°; the overall symmetry of I is therefore C_2. The geometry about each platinum atom is nearly square planar. The two Pt(I) atoms in **1**, **2**, and **3** are bonded with Pt–Pt distances of 2.579 (1), 2.605 (1), and 2.569 (3) Å, respectively. These distances fall within the range of other Pt(I)–Pt(I) separations in other complexes which correspond to

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(2) Crystals of **1** were obtained by slow evaporation (2 weeks) of a solution containing K_2PtCl_4 (25 mg), $NaOCH_3$ (30 mg) in MeOH (30 mL), DMSO (6 mL), and DMF (1 mL) in an open beaker. Compound **2** was obtained by using the same reactants but with 6 mL of DMF. Crystals of **3** were obtained by recrystallization of **2** from CH_2Cl_2. All solvents were used undried. The bright orange crystals were collected and washed with small amounts of acetone and dried under vacuum.

(3) Compound **1**: $[Pt_4O_2Cl_2(DMSO)_6]\cdot 2H_2O$; space group $P2_1/c$, $a = 9.960$ (1) Å, $b = 17.315$ (2) Å, $c = 20.588$ (2) Å, $\beta = 100.73$ (3)°, $V = 3488$ (1) Å^3, $d_{calcd} = 2.644$ g cm^{-3}, $Z = 4$, $R = 0.059$, $R_w = 0.068$. Compound **2**: $[Pt_4O_2Cl_2(DMSO)_6]\cdot DMF\cdot H_2O$; space group $P\bar{1}$, $a = 11.591$ (1) Å, $b = 14.509$ (2), $c = 10.697$ (1) Å, $\alpha = 90.35$ (3), $\beta = 95.78$ (3), $\gamma = 93.77$ (2)°, $V = 1786$ (1) Å^3, d(calcd) = 2.684 g cm^{-3}, $Z = 2$, $R = 0.046$, $R_w = 0.053$. Compound **3**: $[Pt_4O_2Cl_2(DMSO)_6]\cdot CH_2Cl_2$; space group $P\bar{1}$, $a = 11.109$ (1), $b = 16.184$ (2), $c = 10.121$ (1) Å, $\alpha = 94.43$ (3), $\beta = 97.72$ (3), $\gamma = 72.04$ (3)°, $V = 17\ 14$ (1) Å^3, d(calcd) = 2.784 g cm^{-1}, $Z = 2$, $R = 0.058$, $R_w = 0.071$.

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