Table I

biradical	X	R_1	R_2	MeOH		heptane	
				τ,[a] ns	λ_{max}, nm	τ,[a] ns	λ_{max}, nm
1a	O	Ph	Ph	4.9 ± 1.5[b]	320–330 (br)	6.4 ± 1.6[b]	330
1b	O	Ph	H	1.3	305	1.7	~300
1c	CH_2	Ph	Ph	222 ± 18[c]	330	113 ± 13	330
1d	CH_2	Ph	H	146 ± 18[c]	310	55 ± 8	315
1e	CHPh	Ph	H	95			
1f	CH_2	CH_3	H	93[d]	~320	38[e]	
1g	CH_2	OCH_3	H	70 ± 5	~310	30 ± 6[f]	

[a] Confidence limits where given are twice the standard deviation of repetitive samples from the mean. [b] In the presence of 0.05–0.5 M isoprene; lifetime independent of isoprene concentration. [c] Unaffected (±10%) by the presence of 0.1 M isoprene. [d] This work. [e] Small, R. D.; Scaiano, J. C. *Chem. Phys. Lett.* 1977, *59*, 431–434. [f] A substantial fluorescence, probably derived from a trace impurity, is difficult to time resolve in heptane and renders this value less certain than the rest.

increasing number of phenyl groups: **1f** < **1d** < **1c**. Phenyl groups may increase the lifetime by conjugation with the odd electron at the terminus. Increased delocalization should increase the average distance between the unpaired electrons, thus decreasing spin–orbit coupling.[7] The comparison of **1a** and **1b** follows similarly. The β-phenyl in **1e**[8] appears to shorten its lifetime in comparison to **1d**. We hypothesize that conformational factors are involved. We would expect a larger proportion of the conformation with gauche termini, which brings the termini closer than when trans and thus could increase spin–orbit coupling.[7]

If the short lifetimes for **1a** and **1b** are not due to the phenyl groups, the explanation must derive from the presence of the oxygen in the chain. That the effect is very largely specific to the β position is shown by the lifetime of **1g**. The latter, derived from γ-methoxybutyrophenone,[2] has already been reported to have a $k_{Q}\tau$ value similar to that of **1f** from thiol trapping experiments.[11] The present results show a lifetime for **1g** only some 25% shorter than for **1f**. The lifetime of **1h** ($X = CH_2$, R_1 = Ph, R_2 = OH) of 84 ns in methanol[9] represents another example of oxygen at a terminus but not between the termini, and again the effect is small.

A probable contributor to the lifetime-shortening effect of β-O- is the decreased average distance between the unpaired electrons due to the resonance form shown below. Other more speculative

explanations might derive from conformations which provide an angle of approximately 90° between the oxygen 2p orbital and the half-filled p orbital at the adjacent terminus. Such conformations will provide maximal spin–orbit coupling.[7] However, since **1g** presumably could also access analogous conformations, we think at present that the latter explanation is unlikely.

The biradicals **1a** and **1b** are in fact the Paterno–Buchi (preoxetane) biradicals which would formally result from addition of benzophenone and benzaldehyde, respectively, to acetophenone enol. We have studied the transient spectroscopy of benzophenone in the presence of tetramethylethylene and ethyl vinyl ether and observe strong signals in the UV region (λ_{max} 330 nm), with lifetimes roughly 1.5–4 ns depending on olefin and conditions. We assign these as the corresponding Paterno–Buchi biradicals[12] and are gratified at the similarity of lifetime and λ_{max} with expectation, on the basis of **1a** and **1b**. Finally, we note that Peters[13] has recently obtained nearly identical results for another Paterno–Buchi biradical. The combination of all these results renders a recent[14] assignment of a 6–25-μs transient on irradiation of benzophenone and 3-methyl-2-pentene as the corresponding Paterno–Buchi biradical unlikely.

Acknowledgment. We thank the National Science Foundation (Grant CHE7915228) and the Robert A. Welch Foundation (Grant AT-532) for financial support. Flash kinetic work was performed at the Center for Fast Kinetics Research at The University of Texas at Austin, supported by NIH Grant RR-0086 from The Biotechnology Branch of the Division of Research Resources and The University of Texas. We thank M. A. J. Rodgers, D. C. Foyt, and J. Lynch for assistance.

Registry No. 1a, 80326-01-8; **1b**, 80326-02-9; **1c**, 80326-03-0; **1d**, 80326-04-1; **1e**, 80326-05-2; **1f**, 73461-73-1; **1g**, 34903-03-2.

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(7) An excellent review of the precepts for spin–orbit coupling applied to biradicals is given in: Salem, L; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111.

(8) Photochemistry of β,γ-diphenybutyrophenone: Caldwell, R. A.; Fink, P. M. *Tetrahedron Lett.* **1969**, 2987–2989. Wagner, P. J.; Kelso, P. A. *Ibid.* **1969**, 4151–4153.

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Application of the Energy Gap Law to the Decay of Charge-Transfer Excited States

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We recently reported the preparation of a series of osmium(II) polypyridyl compounds.[1] The compounds were remarkable because of the suggestion that the properties of their metal-to-ligand charge-transfer [MLCT; $Os^{II} \rightarrow \pi^*$(bpy) or (phen)] excited states including luminescence lifetimes, emission maxima, and redox potentials are systematically variable by making chemical changes. We have now prepared a more extensive series of compounds and with the extended series are able to identify systematic variations in both nonradiative (k_{nr}) and radiative rate constants (k_r), and the systematic variations have important implications for transition-metal photochemistry.

Table I gives some relevant excited-state parameters for a series of mono- and bis-2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) complexes of Os(II). The complexes were prepared by synthetic routes similar to those reported earlier.[1] They were characterized by UV–visible spectra, cyclic voltammetry, and elemental analyses.[2] Emission maxima reported in Table I are corrected for detector sensitivity.[3a] Integrated emission quantum

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(2) Kober, E. M.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J., manuscript in preparation.

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Table I. Excited-State Parameters for the Two Series of Osmium(II) Polypyridyl Complexes[a]

	A = 2,2'-bipyridine				A = 1,10-phenanthroline			
complex[b]	E_{em}, 10^3 cm^{-1}	ϕ_{em}	k_r s^{-1}	k_{nr} s^{-1}	E_{em} 10^3 cm^{-1}	ϕ_{em}	k_r, s^{-1}	k_{nr}, s^{-1}
$OsA(py)_4^{2+}$					12.89	0.00336	3.65×10^4	1.08×10^7
$OsA_2(py)_2^{2+}$					13.40	0.00817	5.72×10^4	6.94×10^6
$OsA_2(bpy)^{2+}$	13.40	0.00462	7.71×10^4	1.66×10^7				
$OsA_2(phen)^{2+}$	13.51	0.00773	1.03×10^5	1.32×10^7	13.89	0.0159	6.05×10^4	3.76×10^6
cis-$OsA_2(CO)Cl^+$	14.29	0.00168	1.83×10^4	1.09×10^7	14.29	0.00684	1.61×10^4	2.34×10^6
$OsA_2(CH_3CN)_2^{2+}$	14.12	0.0132	8.39×10^4	6.29×10^6	14.54	0.0437	8.84×10^4	1.94×10^6
cis-$A_2Os(CH_3CN)(PMePh_2)^{2+}$	14.66	0.0142	6.71×10^4	4.67×10^6				
trans-$OsA_2(PMe_2Ph)_2^{2+}$					14.88	0.0872	2.21×10^5	2.32×10^6
trans-$OsA_2(PPh_2Me)_2^{2+}$	14.92	0.0622	2.3×10^5	3.47×10^6				
trans-$OsA_2(PPh_3)_2^{2+}$	14.97	0.0827	2.17×10^5	2.41×10^6				
$OsA_2(diars)^{2+}$[c]	14.66	0.0193	1.28×10^5	6.49×10^6	15.04	0.0605	9.95×10^4	1.55×10^6
$OsA_2(Ph_2P(CH_2)_3PPh_2)^{2+}$					15.85	0.135	1.34×10^5	7.51×10^5
$OsA_2(Ph_2PCH_2PPh_2)^{2+}$	15.53	0.0556	1.85×10^5	3.15×10^6	16.03	0.151	1.34×10^5	7.51×10^5
cis-$OsA_2(PPh_2Me)_2^{2+}$	15.11	0.0255	9.77×10^4	3.73×10^6				
trans-OsA_2(*trans*-dpp-ene)$_2^{2+}$[d]	15.11	0.0598	1.54×10^5	2.42×10^6				
$OsA_2(Ph_2PCH_2CH_2PPh_2)^{2+}$	15.63	0.0550	1.19×10^5	2.04×10^6	16.13	0.138	7.53×10^4	4.71×10^5
$OsA_2(dppb)^{2+}$[c]	15.72	0.0492	1.43×10^5	2.76×10^6				
OsA_2(*cis*-dpp-ene)$^{2+}$[d]	15.87	0.0699	1.40×10^5	1.86×10^6	16.42	0.239	1.30×10^5	4.14×10^5
$OsA_2(Ph_2AsCH_2CH_2AsPh_2)^{2+}$					16.08	0.121	7.93×10^4	5.76×10^5
$OsA(diars)_2^{2+}$[c]	16.89	0.265	1.61×10^5	4.48×10^5	17.37	0.361	1.48×10^5	8.35×10^4
$OsA_2(Me_2SO)_2^{2+}$	17.39	0.383	2.55×10^5	4.11×10^5				

[a] k_{nr} is the radiationless decay rate, k_r is the radiative decay rate, ϕ_{em} is the quantum yield for emission, and E_{em} is the corrected emission energy maximum. [b] As PF_6^- salts, all measurements made in deoxygenated CH_3CN solution at 23 ± 2 °C. [c] diars = 1,2-bis(dimethylarsino)benzene. [d] dpp-ene = 1,2-bis(diphenylphosphino)ethylene. [e] dppb = 1,2-bis(diphenylphosphino)benzene.

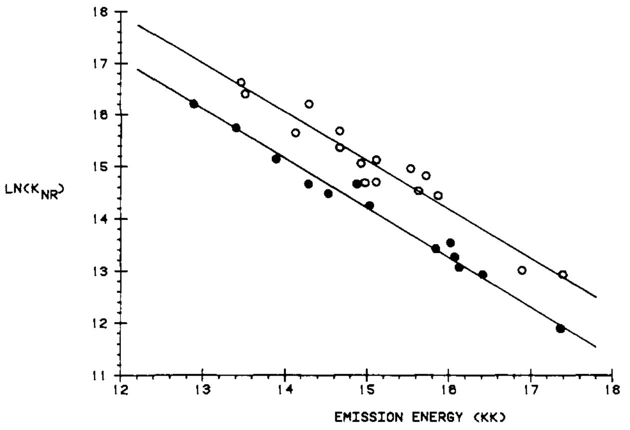

Figure 1. Plot of ln k_{nr} vs. E_{em} for the bpy and phen compounds in Table I (● = phen, ○ = bpy).

yields, ϕ_{em}, were determined in dry, deoxygenated CH_3CN solution at 23 ± 2 °C relative to $[Ru(bpy)_3](PF_6)_2$ as a standard (ϕ_{em} = 0.062).[3b] Luminescence lifetimes were obtained by laser flash photolysis as described previously.[4]

The most important aspect of the data in Table I is the wide (almost two orders of magnitude) variation in the values of k_{nr} for each series of complexes. The radiationless decay constants increase as the emission maxima, E_{em}, shift to lower energies. Figure 1 shows plots of ln k_{nr} vs. the corrected emission maxima for both series. The linear increase of ln k_{nr} with emission energy is in obvious agreement with the energy gap law for radiationless transitions.[5,6]

In essence, the energy gap law predicts that for a series of related excited states based on the same chromophore, radiationless decay rates are determined largely by vibrational overlap between the ground and excited states. Because of the "energy disposal" nature of the process, overlap considerations favor high-frequency vibrations and the application of a low-temperature limit. The extent of vibrational coupling is determined by the magnitude of vibrational wave function overlap between v = o levels in the excited state and highly vibrationally excited isoenergetic levels of the ground state. Using the expression derived by Englman and Jortner,[5] the value of k_{nr} in the low-temperature, weak vibrational coupling limit ($S \leq 1$; note below) is given approximately by eq 1. In eq 1 ΔE is the internal energy gap between the upper

$$k_{nr} = \left(\frac{2\pi V^2}{\hbar}\right)\left(\frac{1}{2\pi\hbar\omega_M\Delta E}\right)^{1/2} \exp(-S)\exp\left(\frac{-\gamma\Delta E}{\hbar\omega_M}\right) \qquad (1)$$

and lower states, ω_M is the frequency of the deactivating mode or modes, and V is the electron tunneling matrix element. The terms γ and S are defined in eq 2 and 3, respectively, and Δ_j is

$$\gamma = \ln\left(\frac{2\Delta E}{\sum_j \hbar\omega_j\Delta_j^2}\right) - 1 \qquad (2a)$$

$$\gamma \sim \ln\left(\frac{2\Delta E}{\hbar\omega_M\Delta_M^2}\right) - 1 \qquad (2b)$$

$$S = \tfrac{1}{2}\sum_j \Delta_j^2 \qquad (3)$$

the dimensionless fractional displacement between the equilibrium nuclear configuration of the ground and excited state for the complex's jth normal mode. Only if the critical high-frequency mode M undergoes substantial distortion in the excited state, as appears to be the case here (see below), can eq 2a be simplified to the form shown in eq 2b.

In comparing a series of related excited states, if the deactivating mode or modes remain common and if variations in V and in S are relatively small, eq 1 can be written in simplified form as eq 4 where it has been assumed that $\Delta E \sim E_{em}$.[7-10] Since ln β and

$$\ln k_{nr} = (\ln\beta - S) - (\gamma E_{em}/\hbar\omega_M) \qquad (4)$$

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(3) (a) Emission maxima corrections were performed with programs and data supplied with the SLM 8000 Photon Counting Spectrofluorimeter used in these experiments. (b) Caspar, J. V., unpublished results.

(4) Nagle, J. K. Ph. D. thesis, University of North Carolina at Chapel Hill, 1979.

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(6) (a) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187. (b) Henry, B. R.; Siebrand, W. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley: New York, 1973; Vol. I. (c) Fong, F. K. "Theory of Molecular Relaxation"; Wiley: New York, 1975.

(7) In fact, $E_{em} = \Delta E - \chi$, where χ includes contributions from both intramolecular (χ_i) and medium vibrations (χ_o).[8] To a first approximation, $E_{em} \sim \Delta E$,[9] but substitution of E_{em} for ΔE does lead to the introduction of a solvent dependence which can be observed experimentally.[10]

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γ are weakly varying functions of ΔE, it can be predicted on the basis of eq 4 that if the assumptions made above are appropriate, a linear relation should exist between ln k_{nr} and E_{em}. From the results shown in Figure 1 there is obvious agreement between theory and experiment. The agreement is not surprising given the assumptions involved and the nature of the excited states. The excited states appear to share a common deactivating mode. The results of investigations of low-temperature emission spectra of Os(bpy)$_3^{2+}$ and several related complexes of the type Os(bpy)$_2$L$_2^{2+}$ [3b,11] all show vibrational progressions of approximately 1300 cm^{-1} corresponding to ligand-based skeletal stretching vibrations[12] and appear to be the dominant deactivating modes, ω_M.[13] The assumption of a low-temperature limit is clearly appropriate for a vibration having $\hbar\omega_M = 1300$ cm^{-1} since $\hbar\omega_M/k_BT > 6$.[5a]

Inherent in the success of eq 4 is the assumption that variations in V are relatively small for the series of excited states. Clearly, V will not be constant, but it appears in the intercept as ln V^2. Variations in V, which are in the range ca. 30–100 cm^{-1} from eq 1, must be too small to affect the linear relationship between ln k_{nr} and E_{em} noticeably. The importance of significant changes in V may appear in the enhanced lifetimes in Table I for phen complexes compared to analogous bpy complexes. The lifetime enhancements of approximately a factor of 3 are almost entirely due to the faster radiationless decay of the bpy excited states. The similarity in slopes in Figure 1 suggests similar deactivating modes and S values for the two series and that radiationless decay rate differences come from a decrease in the electron tunneling matrix element for the phen complexes.

A third assumption is that S, which is a measure of excited-state distortion in the deactivating mode or modes, is constant. Preliminary Franck–Condon analyses on the emission spectra of these complexes using standard procedures[15] show that systematic variations in Δ_M^2 and hence in S do occur as E_{em} increases. However, the variations are relatively small and act only to modify slightly the observed slopes and intercepts of the plots of ln k_{nr} vs. E_{em} and not the conclusions reached here. Further work on the quantitative evaluation of V, Δ_M^2, and S is currently in progress.

The smaller but still significant variations in the radiative rate constants in Table I should also be noted since it is their interplay with k_{nr} which determines excited-state lifetimes. In particular, as the luminescence is moved to higher energy, k_r becomes more important in determining excited-state lifetimes. Radiative decay rate constants are predicted to increase approximately as the cube of the emission energy, provided that the integrated intensity of the charge-transfer absorption remains constant.[16] The data in Table I are in agreement with this prediction, and it appears that there exist satisfactory theoretical bases for accounting in a detailed way for relative excited-state lifetimes in this series of compounds.

Acknowledgment is made to the Department of Energy under Grant DE-A505-78ER06034 for support of this research, the Morehead Foundation for a fellowship for E.M.K., and Dr. Ephraim Buhks for some helpful comments.

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[13] We have prepared several complexes using fully deuterated bipyridine and find only small isotope effects upon k_{nr}, indicating that C–H stretching vibrations which frequently act as deactivating modes in organic systems[14] are not the principal active modes here.

[14] (a) Griesser, H. J.; Wild, U. P. *Chem. Phys.* **1980**, *52*, 117. (b) Siebrand, W. In "The Triplet State"; Cambridge University Press, New York, 1967. (c) Byrne, J. P.; McCoy, E. F.; Ross, I. G. *Aust. J. Chem.* **1965**, *18*, 1589.

[15] (a) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. (b) Ballhausen, C. J. "Molecular Electronic Structures of Transition Metal Complexes"; McGraw-Hill, New York, 1979.

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On Coupling Carbenes and Carbynes

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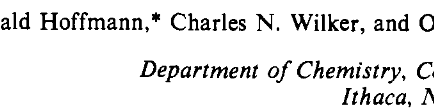
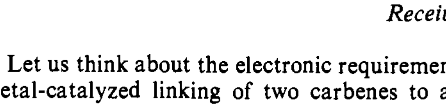
Let us think about the electronic requirements for transition-metal-catalyzed linking of two carbenes to an olefin, **1**, two carbynes to an acetylene, **2**, or the reverse reaction, the direct dismantling of a coordinated ethylene or acetylene. A wide range of coordination numbers and geometries could be envisaged, but the essence of the reactions is revealed by examining the naked metal case and then restoring the other ligands. Figure 1 shows a level correlation diagram for reaction 1 for M = W and no ligands. The two methylenes are put in a conformation appropriate to the final geometry of the coordinated olefin.[1]

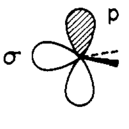


1



2

Each methylene contributes a σ and p orbital, **3**.[2] Two methylenes bring to M(CH$_2$)$_2$ in- and out-of-phase combinations of these σ and p orbitals. Three of these four combinations find a metal partner to interact with—they are 1a$_1$, 1b$_2$, 2a$_1$ as seen in Figure 1. The fourth combination, 2b$_2$, **4**, having too many nodes, is of the wrong pseudosymmetry to interact effectively with any metal s, p, or d orbital. Above these four orbitals lie three metal d's, unaffected by the methylenes. Higher still are some metal–carbene antibonding combinations, 4a$_1$, 3b$_2$, 5a$_1$, hybridized at the metal to point away from the carbenes.



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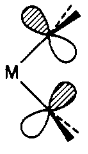

4

On the olefin side we have 1a$_1$, the CC σ bond, and 2a$_1$ and 1b$_2$, the two combinations responsible for metal–olefin bonding. Note the π and π^* components here.[3] Above these lie four metal orbitals as well as 2b$_2$ and 5a$_1$, antibonding partners to 1b$_2$ and 2a$_1$.

The level correlations are straightforward. The critical orbital, 2b$_2$, is carbene–carbene antibonding. As the carbenes near each other, this level goes up in energy, sharply so. It must correlate to a CC σ^* or π^* level, and no metal mixing can assuage its destabilization. Metal interaction can keep one b$_2$ orbital (1b$_2$) down in energy but not two.

At this point a convention for electron counting must be established. If the carbenes and the olefin are treated as neutral,

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[1] This may not necessarily be the equilibrium orientation of the two carbenes—that being set by either steric factors (as it seems to be in the known biscarbene complexes, to be referenced later) or by electronic factors: the two acceptors will avoid, if possible, competing for the same metal d orbital. See, for instance: Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112–2120 and references therein. Be that as it may, the ethylene precursor geometry must be attained early on in the reaction.

[2] See: Harrison, J. F. In "Carbene Chemistry", 2nd Ed.; Kirmse, W., Ed.; Academic Press: New York, 1971; pp 159–193.

[3] For a general discussion of L$_n$M(ethylene) complexes, see: Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320. Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *Ibid.* **1979**, *101*, 3801–3812.

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