J. Am. Chem. Soc. **1982**, *104*, 3804–3812

Photophysics and Photochemistry of Pentacarbonyl(pyridine)tungsten(0) Complexes Which Luminesce in Fluid Solution

Alistair J. Lees and Arthur W. Adamson*

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007.

Received August 12, 1981

Abstract: Luminescence data are reported for $W(CO)_5L$ complexes, where L = 4-acetylpyridine, 4-benzoylpyridine, 4-cyanopyridine, and 4-formylpyridine, as solids and in fluid solution. Photosubstitution quantum yields (for the dissociation of L) have been recorded for these $W(CO)_5L$ complexes in several solvents with various irradiation wavelengths. Apparent activation energies for the $W(CO)_5L$ complexes in several solvents have been measured from the temperature dependencies of the emission and photoreactivity processes. Quenching of the emission and photoreactivity processes is reported for several quenchers; the results are used to bracket the energies of the emitting state for each complex. Two low-lying metal-to-ligand charge-transfer excited states are implicated in the radiative decay process. Possible excited-state schemes for these $W(CO)_5L$ complexes are discussed in accordance with the experimental observations. Excited-state absorption and primary photoproduct spectra have been recorded for the $W(CO)_5L$ complexes in methylcyclohexane and benzene by monitoring techniques. A common photoproduct is inferred, its spectrum being close to that of $W(CO)_5S$, where S denotes solvent, following pulse laser photolysis of $W(CO)_6$ as previously reported by us.

Following initial studies by Strohmeier and co-workers[1-5] the photochemical behavior of group 6B metal carbonyls and their derivatives has been the subject of numerous investigations.[6-21] Many of the early papers were centered around the photolysis of the parent hexacarbonyls in solution and as rigid glasses. More recently, conventional flash photolysis techniques have provided information about intermediates produced in these photolyses.[22-27]

Of current interest[28] is the photochemistry of metal complexes having low-lying metal-to-ligand charge-transfer (MLCT) excited states,[29-41] particularly substituted mononuclear metal carbonyls.[42-59] Complexes of the general formula $W(CO)_5L$, where

---

(1) Strohmeier, W.; von Hobe, D. *Chem. Ber.* **1961**, *94*, 761–765.

(2) Strohmeier, W.; Gerlach, K. *Chem. Ber.* **1961**, *94*, 398–406.

(3) Strohmeier, W.; von Hobe, D. *Chem. Ber.* **1961**, *94*, 2031–2037.

(4) Strohmeier, W.; Gerlach, K.; von Hobe, D. *Chem. Ber.* **1961**, *94*, 164–168.

(5) Strohmeier, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730–737.

(6) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *J. Am. Chem. Soc.* **1962**, *84*, 3589–3590.

(7) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *J. Am. Chem. Soc.* **1963**, *85*, 1013–1014.

(8) Dobson, G. R. *J. Phys. Chem.* **1965**, *69*, 677–678.

(9) Koerner von Gustorf, E.; Grevels, F.-W. *Fortschr. Chem. Forsch.* **1969**, *13*, 366–450 and references therein.

(10) Schwenzer, G.; Darensbourg, M. Y.; Darensbourg, D. *J. Inorg. Chem.* **1972**, *11*, 1967–1970.

(11) Graham, M. A.; Rest, A. J.; Turner, J. J. *J. Organomet. Chem.* **1970**, *24*, C54–C56.

(12) Graham, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2939–2948.

(13) Perutz, R. N.; Turner, J. J. *J Am. Chem. Soc.* **1975**, *97*, 4791–4800.

(14) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271–285.

(15) Wrighton, M.; Hammond, G. S.; Gray, H. B. *Mol. Photochem.* **1973**, *5*, 179–193.

(16) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401–430.

(17) Wrighton, M. *Inorg. Chem.* **1974**, *13*, 905–909.

(18) Hughey, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440–4441.

(19) Darensbourg, D. J.; Murphy, M. A. *Inorg. Chem.* **1978**, *17*, 884–888.

(20) Darensbourg, D. J.; Murphy, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 463–468.

(21) Black, J. D.; Braterman, P. S. *Inorg. Chim. Acta* **1980**, *44*, L181–L182.

(22) McIntyre, J. A. *J. Phys. Chem.* **1970**, *74*, 2403–2404.

(23) Nasielski, J.; Kirsch, P.; Wilputte-Steinert, L. *J. Organomet. Chem.* **1971**, *29*, 269–274.

(24) Kelly, J. M.; Hermann, H.; Koerner von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105–106.

(25) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259–269.

(26) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220–1221.

(27) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381–4384.

(28) See, for example: Mann, K. R.; Gray, H. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 306–307.

(29) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187–1194.

(30) Ford, P. C.; Struermer, D. H.; McDonald, D. P. *J. Am. Chem. Soc.* **1969**, *91*, 6209–6211.

(31) Chaisson, D. A.; Hintze, R. E.; Stuermer, D. H.; Petersen, J. D.; McDonald, D. P.; Ford, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 6665–6673.

(32) Hintze, R. E.; Ford, P. C. *Inorg. Chem.* **1975**, *14*, 1211–1213.

(33) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601–603.

(34) Ford, P. C. *Rev. Chem. Intermed.* **1979**, *2*, 267–296.

(35) Crosby, G. A.; Hipps, K. W.; Elfring, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 629–630.

(36) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97–105.

(37) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6384–6385.

(38) Lin, C-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536–6544.

(39) Young, R. C.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 286–287.

(40) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.

(41) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496–499.

(42) Gray, H. B.; Billig, E.; Wojcicki, A.; Farona, M. *Can. J. Chem.* **1963**, *41*, 1281–1288.

(43) Herberhold, M.; Brabetz, H. *Chem. Ber.* **1970**, *103*, 3896–3908.

(44) Herberhold, M.; Brabetz, H. *Chem. Ber.* **1970**, *103*, 3909–3917.

(45) Dieck, H. T.; Renk, I. W. *Angew. Chem.* **1970**, *82*, 805–807.

(46) Fischer, E. O.; Kollmeier, H. J.; Kreiter, C. G.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1970**, *22*, C39–C42.

(47) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959–966.

(48) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998–1003.

(49) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405–420.

(50) Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111–1119.

(51) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105–4109.

0002-7863/82/1504-3804$01.25/0

Table I. Absorption Band Maxima for $W(CO)_5L$ Complexes at 298 K

	band maxima λ, nm (ε, M^{-1} cm^{-1}), with the indicated solvents				
L	methylcyclohexane	isooctane	benzene	THF	ethanol
4-ACpy	404 (9650) 442 (9590)	404 (8520) 440 (8310)	402 (9810)	398 (9600)	398 (9540)
4-BNpy	405 (8780) 435 (7790)	405 (7720) 435 (6870)	403 (9530)	398 (9380)	398 (9310)
4-CNpy	404 (7280) 454 (8680)	404 (6180) 455 (7810)	404 (8040)	398 (8390)	398 (8370)
4-FMpy	402 (5990) 470 (7640)	402 (5830) 470 (6850)	402 (7280)	399 (6940)	398 (6850)

Table II. Emission Data[a] for $W(CO)_5L$ Complexes at 298 K

	emission maxima,[b] $\times 10^3$ cm^{-1}			luminescence quantum yield, $\times 10^{-4}$, with two solvents[c]	
		solvent[c]			
L	solid	methylcyclohexane	benzene	methylcyclohexane	benzene
4-ACpy	17.25	16.08	15.90	5.3	1.6
4-BNpy	18.75	16.23	16.42	7.7	2.3
4-CNpy	16.80	15.88	15.54	2.2	1.3
4-FMpy	16.60	15.85	15.38		1.0

[a] The excitation wavelength is 400 nm. [b] Corrected for variation in photomultiplier response as a function of wavelength. [c] 5-8 × 10^{-5} M deaerated solutions.

L is an oxygen or nitrogen donor, have intriguing spectroscopic and photochemical characteristics. In rigid glasses at 77 K they luminesce, the emission having been assigned to either a $^3E \rightarrow {}^1A_1$ ligand-field (LF) transition or a W → L charge-transfer (CT) transition, depending on the nature of L.[51,60,61] The electronic absorption spectra indicate that as L becomes more electron withdrawing, the CT state lowers in energy and for various substituted pyridines as L has been inferred to be the lowest lying state.[51] The W → L CT state has been shown to be significantly less reactive than the lowest LF state for substitution of L in $W(CO)_5L$ complexes, analogous to previous findings for $Ru(NH_3)_5L^{2+}$ complexes.[29-34] Therefore, in the cases of $W(CO)_5L$ complexes where a W → L CT absorption is the lowest energy absorption, the photosubstitution quantum yield of L in $W(CO)_5L$ is relatively low. Correspondingly, the luminescence from $W(CO)_5L$ complexes in EPA at 77 K was found to shift to lower energy maxima and to show an increase in emission lifetime with increasing electron-withdrawing effect of L. This was the case for $W(CO)_5L$ complexes where L = 4-ACpy (4-acetylpyridine), 4-BNpy (4-benzoylpyridine), 4-CNpy (4-cyanopyridine), and 4-FMpy (4-formylpyridine).[51]

$W(CO)_5L$ complexes were not thought to luminesce in room-temperature solutions, presumably because of rapid ligand dissociation and nonradiative decay to the ground state. However, recently we have observed emission from $W(CO)_5$(4-CNpy) in room-temperature solution and the quenching of emission and photosubstitution reactivity by anthracene.[62] As a consequence, a complete study of the photochemistry and photophysics of $W(CO)_5L$ complexes has been undertaken, the results of which are reported here.

Results

Synthesis of $W(CO)_5L$. $W(CO)_5L$ complexes were prepared either directly (reaction 1) or via the tetrahydrofuran complex, $W(CO)_5(THF)$ (reactions 2 and 3), according to a literature procedure.[5,9] Reaction 1 was used to prepare $W(CO)_5L$, where

$$W(CO)_6 \xrightarrow[\substack{L \\ \text{Ar purged} \\ \text{methylcyclohexane}}]{h\nu} W(CO)_5L + CO \quad (1)$$

$$W(CO)_6 \xrightarrow[\substack{\text{Ar purged} \\ \text{THF}}]{h\nu} W(CO)_5(THF) + CO \quad (2)$$

$$W(CO)_5(THF) \xrightarrow[L]{\Delta} W(CO)_5L + THF \quad (3)$$

L = pyridine, piperidine, diethylmethylamine, triethylamine, 2,4,6-trimethylpyridine, 2-acetylpyridine, 4-acetylpyridine, 2-benzoylpyridine, 4-benzoylpyridine, 4-cyanopyridine, 4-formylpyridine, acetone, diethyl ether, ethanol, and 1-pentene. A major limitation of this procedure, however, is that during production of $W(CO)_5L$ secondary photochemical reactions can take place which may lead to other substituted products. The route involving prior photogeneration of the tetrahydrofuran complex, $W(CO)_5(THF)$ (reactions 2 and 3), has considerable precedence, as it largely avoids secondary photolysis products. Reactions 2 and 3 were used to prepare $W(CO)_5L$, where L = pyridine, piperidine, 4-acetylpyridine, 4-benzoylpyridine, 4-cyanopyridine, and 4-formylpyridine, and the products were isolated as solid complexes.

Electronic Absorption Spectra. Absorption spectra in the 300–600-nm region for $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), $W(CO)_5$(4-CNpy), $W(CO)_5$(4-FMpy), and $W(CO)_6$ in methylcyclohexane are shown in Figure 1a. A comparison of the absorption spectra of $W(CO)_5$(4-CNpy) in methylcyclohexane and 1:1 (v/v) methylcyclohexane–benzene is illustrated in Figure 1b. Absorption spectral data for the complexes studied are summarized in Table I.

Luminescence Data. Corrected emission spectra for $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), $W(CO)_5$(4-CNpy), and $W(CO)_5$(4-FMpy) as solids and in methylcyclohexane and benzene at 298 K are shown in Figure 2. The band maxima and luminescence quantum yields are summarized in Table II. The emission spectra at 298 K were found to be independent of excitation wavelength; the emission from $W(CO)_5$(4-CNpy) was

---

(52) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597–1598.

(53) Vliek, R. M. E.; Zandstra, P. J. *Chem. Phys. Lett.* **1975**, *31*, 487–491.

(54) Blakney, G. B.; Allen, W. F. *Inorg. Chem.* **1971**, *10*, 2763–2770.

(55) Frazier, C. C.; Kisch, H. *Inorg. Chem.* **1978**, *17*, 2736–2744.

(56) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154–3161.

(57) Dahlgren, R. M.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 1448–1454.

(58) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1979**, *18*, 597–602.

(59) Boxhoorn, G.; Oskam, A.; Gibson, E. P.; Narayanaswamy, R.; Rest, A. J. *Inorg. Chem.* **1981**, *20*, 783–786.

(60) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 4336–4337.

(61) Wrighton, M.; Hammond, G. S.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 3122–3124.

Table III. Solvent and Temperature Dependence of Emission Lifetime for $W(CO)_5L$ Complexes

		emission lifetime,[a] μs					
			solvent[b]				
temp, K	L	solid	methylcyclohexane	isooctane	benzene	THF	ethanol
278	4-ACpy	1.401	0.554	0.562	0.258	0.057	0.028
	4-BNpy	1.638	0.621	0.577	0.235	0.043	0.027
	4-CNpy	2.326	0.438	0.435	0.269	0.075	0.034
	4-FMpy	0.528	0.333	0.359	0.139	0.040	0.025
283	4-ACpy	1.305	0.519	0.532	0.243	0.048	0.026
	4-BNpy	1.529	0.587	0.520	0.222	0.034	0.025
	4-CNpy	2.167	0.422	0.385	0.250	0.069	0.031
	4-FMpy	0.501	0.313	0.341	0.133	0.038	0.023
288	4-ACpy	1.224	0.496	0.484	0.225		
	4-BNpy	1.439	0.538	0.480	0.213		
	4-CNpy	2.066	0.398	0.355	0.233		
	4-FMpy	0.480	0.293	0.320	0.124		
293	4-ACpy	1.142	0.457	0.439	0.211		
	4-BNpy	1.344	0.505	0.441	0.199		
	4-CNpy	1.944	0.389	0.327	0.219		
	4-FMpy	0.462	0.273	0.307	0.115		
298	4-ACpy	1.072	0.428	0.390	0.197		
	4-BNpy	1.269	0.459	0.418	0.190		
	4-CNpy	1.822	0.360	0.297	0.202		
	4-FMpy	0.433	0.251	0.280	0.109		
303	4-ACpy	1.011	0.393	0.352	0.189		
	4-BNpy	1.193	0.430	0.384	0.177		
	4-CNpy	1.721	0.343	0.269	0.187		
	4-FMpy	0.420	0.234	0.256	0.101		

[a] The excitation wavelength is 353 nm. [b] 4-8 × 10^{-5} M deaerated solutions.

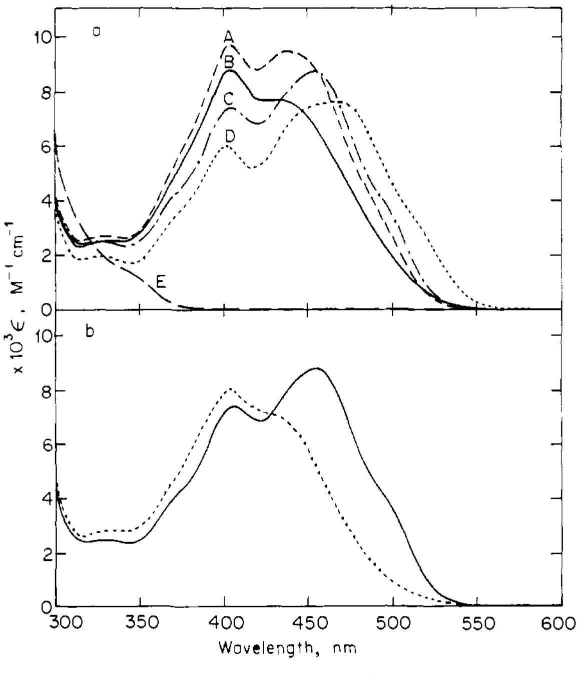


Figure 1. Ligand and solvent effects on the electronic absorption spectra of $W(CO)_5L$ complexes at 298 K. (a) $W(CO)_5L$ in methylcyclohexane, L = 4-ACpy (A), 4-BNpy (B), 4-CNpy (C), 4-FMpy (D), and CO (E). (b) $W(CO)_5$(4-CNpy) in (—) methylcyclohexane and (---) 1:1 (v/v) methylcyclohexane–benzene.

also determined in methylcyclohexane with 530-nm excitation from the Nd glass laser and was the same within experimental error as that shown in Figure 2. For $W(CO)_5$(4-CNpy) in a methylcyclohexane glass at 77 K the emission spectrum and emission lifetime recorded following 353-nm excitation were as reported previously.[51] Emission was not observed from the glass with 530-nm excitation.

Very weak emissions were observed in the 500–600-nm region following pulsed excitation at 353 nm of 5 × 10^{-5}–2 × 10^{-4} M solutions of $W(CO)_5L$ in methylcyclohexane at 298 K, where L = pyridine, piperidine, diethylmethylamine, triethylamine, 2,4,6-trimethylpyridine, 2-acetylpyridine, 2-benzoylpyridine, acetone, diethyl ether, ethanol, and 1-pentene. The emissions from these solutions followed the Nd laser pulse, that is, the lifetimes were less than 10 ns.

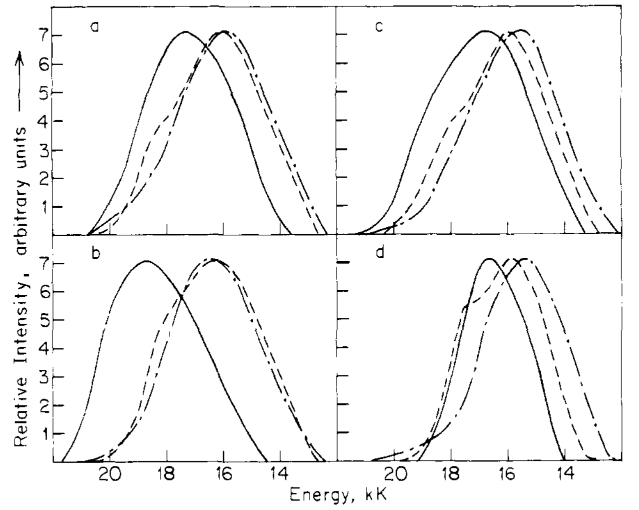


Figure 2. Corrected emission spectra at 298 K of (a) $W(CO)_5$(4-ACpy), (b) $W(CO)_5$(4-BNpy), (c) $W(CO)_5$(4-CNpy), and (d) $W(CO)_5$(4-FMpy); (—) solid, (---) 6–8 × 10^{-5} M $W(CO)_5L$ in methylcyclohexane and (-•-) 4–6 × 10^{-5} M $W(CO)_5L$ in benzene. Excitation wavelength is 400 nm. Intensities are scaled to make maxima equal.

The relative emission intensity of 5.5 × 10^{-5} M $W(CO)_5$(4-ACpy) in methylcyclohexane as a function of temperature was measured with 353-nm excitation. The relative emission intensities at 278, 283, 288, 293, 298, and 303 K are 5.9, 6.3, 7.1, 7.4, 7.7, and 8.5, respectively.

Emission lifetimes (τ) recorded from $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), $W(CO)_5$(4-CNpy), and $W(CO)_5$(4-FMpy) as solids or in solution as a function of temperature are reported

Table IV. Apparent Activation Energy, E^*, and Frequency Factor, A, of W(CO)$_5$L Complexes from Emission Lifetime Data

	apparent activation energy, kcal mol^{-1}				frequency factor, A, $\times 10^8$ s^{-1}			
		solvent				solvent		
L	solid	methyl-cyclohexane	isooctane	benzene	solid	methyl-cyclohexane	isooctane	benzene
A-ACpy	2.2	2.3	3.2	2.2	0.4	1.1	5.8	1.9
4-BNpy	2.1	2.5	2.7	1.9	0.3	1.5	2.5	1.2
4-CNpy	2.0	1.5	3.1	2.4	0.2	0.4	6.6	2.9
4-FMpy	1.6	2.4	2.2	2.2	0.3	2.2	1.5	3.6

in Table III. Emission lifetimes were observed to be the same following either 353- or 530-nm excitation. Plots of ln $1/\tau$ vs. $1/T$ give good Arrhenius behavior for the solid complexes and the solutions studied, the least-squares line being $1/\tau = A \exp(-E^*/RT)$, R in kilocalories; the apparent activation energies (E^*) and frequency factors (A) are shown in Table IV. The activation energies are estimated to be accurate to ±1 kcal mol^{-1}.

The luminescence of 1.4×10^{-2} M benzophenone and 2.5×10^{-1} M biacetyl was quenched by $2–5 \times 10^{-5}$ M W(CO)$_5$(4-ACpy), W(CO)$_5$(4-BNpy), W(CO)$_5$(4-CNpy), and W(CO)$_5$(4-FMpy) complexes in solution. Emission spectra at 293 K were obtained from solutions of (a) 1.4×10^{-2} M benzophenone in benzene and (b) 1.4×10^{-2} M benzophenone with 4.9×10^{-5} M W(CO)$_5$(4-ACpy) in benzene with 353-nm excitation. At these solution concentrations, excitation at 353 nm can be assumed to be entirely into benzophenone. The intensity of the emission spectrum obtained from case a is 3.2 times that obtained from case b, correcting the latter spectrum for the inner filter absorption by the W(CO)$_5$(4-ACpy) complex. The emission lifetimes of the benzophenone emission were found to be (a) 8 μs and (b) 2.5 μs, respectively, with 353-nm excitation. The bimolecular quenching rate constant k_q is calculated to be 5.6×10^9 M^{-1} s^{-1}, using the Stern–Volmer equation, $\tau^0/\tau = 1 + k_q\tau^0[\mathrm{Q}]$. Here, τ^0 is the lifetime in the absence of quencher, τ is the lifetime with quencher present, and [Q] is the quencher concentration.

Emissions from $5–8 \times 10^{-5}$ M solutions of W(CO)$_5$(4-ACpy), W(CO)$_5$(4-BNpy), W(CO)$_5$(4-CNpy), and W(CO)$_5$(4-FMpy) in methylcyclohexane were quenched by the presence of 5×10^{-3} M anthracene, 9-methylanthracene, and 1,2-benzanthracene. Emission from $5–8 \times 10^{-5}$ M solutions of W(CO)$_5$(4-ACpy), W(CO)$_5$(4-BNpy), W(CO)$_5$(4-CNpy), and W(CO)$_5$(4-FMpy) in benzene was quenched by the presence of 5×10^{-3} M acenaphthaquinone. Emission quenching was not observed from solutions of $5–8 \times 10^{-5}$ M W(CO)$_5$(4-ACpy), W(CO)$_5$(4-BNpy), W(CO)$_5$(4-CNpy), and W(CO)$_5$(4-FMpy) containing 5×10^{-3} M chrysene, coronene, benzil, fluoranthene, and 1,2,5,6-dibenzanthracene. The quenching of the emission lifetime of W(CO)$_5$(4-CNpy) by anthracene follows Stern–Volmer kinetics and is shown in Figure 3. The slope k_q corresponds to a bimolecular quenching rate constant of 4.0×10^9 M^{-1} s^{-1}.

Photosubstitution Reactivity. Figure 4 illustrates the spectral sequence accompanying the 465-nm irradiation of (a) W(CO)$_5$(4-ACpy) in methylcyclohexane and (b) W(CO)$_5$(4-BNpy) in methylcyclohexane, showing progression to near zero terminal absorbance in the 450–500-nm region. Before photolysis 0.05 M ethanol was added to each solution; the product in each case is W(CO)$_5$(C$_2$H$_5$OH), apparently uncomplicated by side or subsequent reactions. Quantum yields, ϕ, for this photosubstitution reaction were measured for $5–7 \times 10^{-5}$ M W(CO)$_5$(4-CNpy) as a function of solvent and temperature, using 465-nm irradiation. The results are given in Table I.

Quantum yields were similarly obtained for W(CO)$_5$(4-ACpy) in methylcyclohexane. The values for the above temperatures were 0.016, 0.020, 0.025, 0.030, and 0.040, respectively. The corresponding respective yields for W(CO)$_5$(4-BNpy) were 0.014, 0.018, 0.021, 0.027, and 0.035, also in methylcyclohexane.

An early loss of isosbestic points was observed on photolysis of W(CO)$_5$L solutions not containing at least 0.025 M entering ligand. There was, however, no dependence of either the photosubstitution quantum yield or the emission lifetime on ethanol

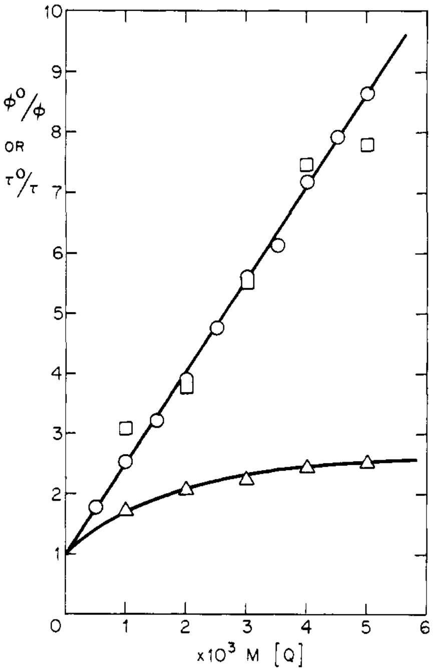


Figure 3. Quenching of 7.5×10^{-5} M W(CO)$_5$(4-CNpy) processes at 298 K by anthracene in methylcyclohexane containing 0.05 M ethanol (○, τ^0/τ; □, ϕ^0/ϕ; △, ϕ^0/ϕ). Excitation wavelengths are (○) 530 nm, (□) 520 nm, and (△) 430 nm.

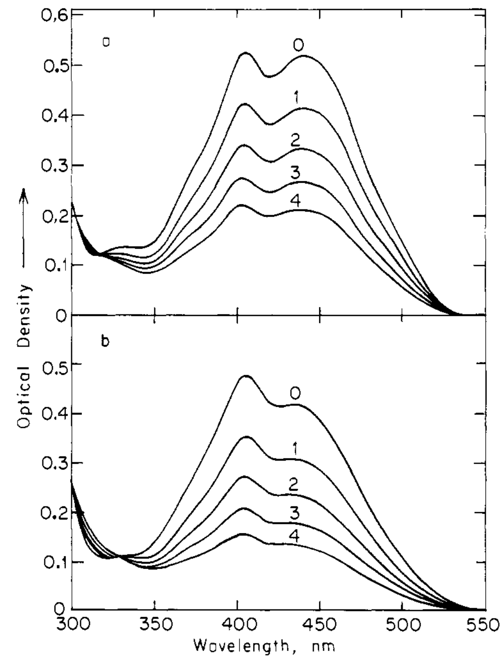


Figure 4. Electronic absorption spectral changes accompanying the 465-nm irradiation (equal time intervals) at 298 K of (a) 5.4×10^{-5} M W(CO)$_5$(4-ACpy) and (b) 5.4×10^{-5} M W(CO)$_5$(4-BNpy) in methylcyclohexane. Both solutions contain 0.05 M ethanol, the entering ligand.

concentration in the 0.025–0.1 M range. Ethanol is thus not a quencher in dilute solution and does scavenge completely the photochemically produced $W(CO)_5$ intermediate. Quantum yields were not obtained for $W(CO)_5$(4-FMpy) in methylcyclohexane because of thermal reaction.

The photosubstitution reactivity of 5.5×10^{-5} M $W(CO)_5$(4-CNpy) in methylcyclohexane containing 0.05 M ethanol was obtained at two other irradiation wavelengths, 430 and 520 nm. At the 520-nm irradiation wavelength, the values of ϕ at 283, 288, 293, 298, and 303 K are 0.011, 0.013, 0.016, 0.021, and 0.026, respectively. These data show good Arrhenius behavior, the least-squares line corresponding to an apparent activation energy of 7.6 ± 1 kcal mol^{-1}. At the 430-nm irradiation wavelength, the yield is again temperature dependent; the values at 283, 288, 293, 298, and 303 K are 0.095, 0.099, 0.110, 0.120, and 0.138, respectively. The least-squares line of an Arrhenius type plot corresponds to an apparent activation energy of 3.2 ± 1 kcal mol^{-1}.

Quenching of the photosubstitution reactivity of $W(CO)_5$(4-CNpy) with anthracene was observed with use of a 520-nm irradiation wavelength, near that used in recording the lifetime quenching data. A Stern–Volmer type plot of ϕ^0/ϕ, where superscript zero denotes the absence of quencher, is linear against anthracene concentration (see Figure 3). The slope is common with the lifetime data, within experimental error, corresponding to a bimolecular rate constant of 4.0×10^9 M^{-1} s^{-1}, about the diffusion-controlled limit.

Quenching of the photosubstitution reactivity of $W(CO)_5$(4-CNpy) with anthracene was also observed with use of a 430-nm irradiation wavelength. Quantum yields were recorded over the first 5% of reaction; this largely avoids a build up of the photoproduct $W(CO)_5(EtOH)$ which absorbs at this wavelength. The quantum yields do not obey Stern–Volmer kinetics (see Figure 3).

Excited-State Absorption and Primary Photoproduct Spectra. Following a 353-nm pulse excitation of 4–8 × 10^{-5} M $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), and $W(CO)_5$(4-CNpy) in methylcyclohexane and benzene the transmitted monitoring beam showed an instantaneous deflection from V_0 to V_{in}, that is, either an increase or decrease which followed the 20-ns laser pulse. Here, V denotes voltage at the oscilloscope signal from the photomultiplier. A measurably slow change then occurred, in which V_t, the intensity at time t after the pulse, either increased or decreased to a final value V_∞. The instantaneous and relatively slow deflections are assigned to excited-state absorption (ESA) and the formation of primary photoproduct (PP), respectively. The extinction coefficients of the excited-state absorption and the primary photoproduct were calculated with use of 4 and 5. C_0 is the

$$\epsilon_{ESA} = \frac{\log (V_0/V_{in}) + 0.9D_0}{0.9C_0} \tag{4}$$

$$\epsilon_{pp} = \frac{\log (V_0/V_\infty) + 0.9D_0}{0.9C_0} \tag{5}$$

concentration of the complex, and D_0 is the optical density at the monitoring wavelength. Equations 4 and 5 correct for the monitoring geometry (see Experimental Section). The actual degree of photolysis by a single laser pulse was essentially 100% in the monitoring volume.

The calculated excited-state absorption spectra for $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), and $W(CO)_5$(4-CNpy) in methylcyclohexane and benzene are shown in Figure 5. The decay of the excited-state absorption for any of the $W(CO)_5L$ complexes was observed to be a single exponential, equal within experimental error to the emission lifetime reported in Table III. The absorption spectra of the primary photoproducts following excitation of $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), and $W(CO)_5$(4-CNpy) in methylcyclohexane and benzene are shown in Figure 6.

Discussion

Electronic Absorption Spectra. The absorption spectra shown in Figure 1 show two distinct absorption maxima (both with $\epsilon > 5 \times 10^3$ M^{-1} cm^{-1}) for each of the $W(CO)_5L$ complexes in methylcyclohexane. The higher-energy absorption-band maxima at 403 nm (± 2 nm) are essentially unshifted by variations in the nature of the substituent on the pyridine ligand and the solvent medium (see Figure 1 and Table I). The lower-energy absorp-

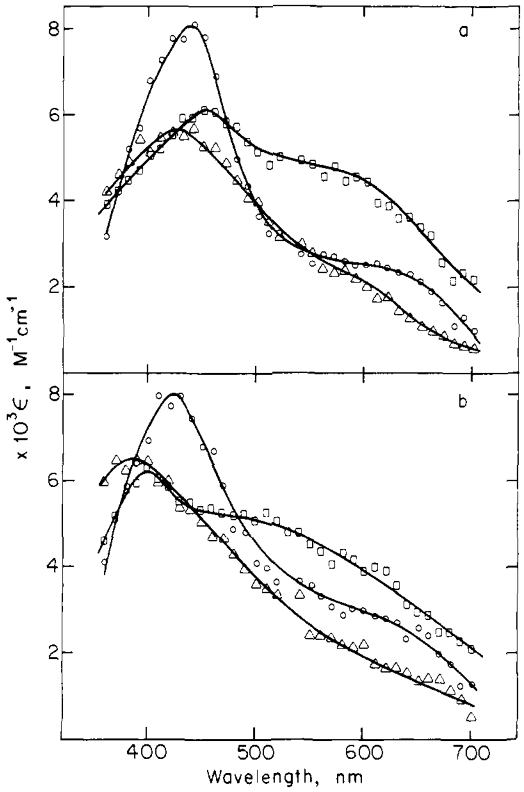


Figure 5. Excited-state electronic absorption spectra at 298 K of (○) $W(CO)_5$(4-ACpy), (□) $W(CO)_5$(4-BNpy), and (△) $W(CO)_5$(4-CNpy) in (a) methylcyclohexane and (b) benzene.

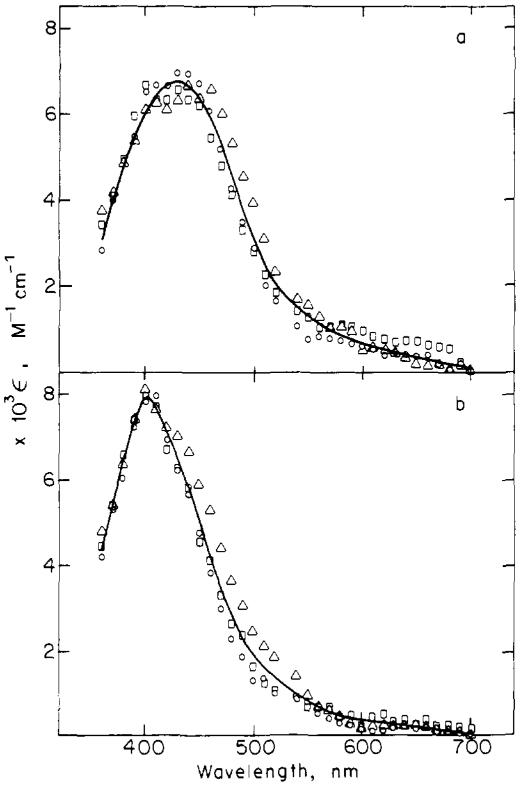


Figure 6. Transient electronic absorption spectra at 298 K following laser pulse photolysis of (○) $W(CO)_5$(4-ACpy), (□) $W(CO)_5$(4-BNpy), and (△) $W(CO)_5$(4-CNpy) in (a) methylcyclohexane and (b) benzene.

tion-band maxima are observed in the range 435–470 nm and their positions illustrate an extraordinary dependence on the nature of ligand substituent and the solvent medium (see Figure 1 and Table I). As the nature of the pyridine ligand substituent becomes more electron withdrawing, that is, as one moves from L = 4-ACpy to L = 4-FMpy, the band undergoes a red shift. In a more polar solvent medium the band appears to reduce in intensity and to blue shift; for the solvents benzene, tetrahydrofuran, and ethanol, this band progressively overlaps with the high energy transition and their maxima becomes indistinguishable (see Table I). These absorption bands at ~403 and 435–470 nm have been previously assigned to a ligand-field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ transition and a metal-to-ligand charge-transfer (MLCT) transition, respectively.[51] Our data support this assignment.

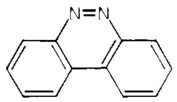
Weaker absorption bands are observed in the $W(CO)_5L$ spectra shown in Figure 1. The maxima at ~330 nm and shoulders at ~370 nm do not shift appreciably with variations of the pyridine ligand substituent and the solvent polarity. These absorption bands are assigned as ligand-field transitions. The low-energy shoulders to the 435–470-nm bands are sensitive to changes in the nature of ligand substituent and solvent polarity. This absorption, in the 490–520-nm range, is therefore again assigned as a metal-to-ligand charge-transfer transition. The use of spin multiplicity designations has been avoided in these assignments because there is expected to be substantial coupling of spin and orbital angular moments for such heavy transition metal complexes.

The energy of an excited state formed immediately following the absorption process can be approximated from the long wavelength tail $\bar{\nu}_{0-0}$ of a broad-band absorption. We have assumed the absorption bands in the $W(CO)_5L$ spectrum to be gaussian in shape and have taken the $\bar{\nu}_{0-0}$ transition to be at $\bar{\nu}_{5\%}$, where absorption intensity at $\bar{\nu}_{5\%}$ = (0.05)(absorption intensity at $\bar{\nu}_{max}$). From the electronic spectra of the $W(CO)_5L$ complexes, where L is 4-ACpy, 4-BNpy, 4-CNpy, and 4-FMpy in methylcyclohexane, isooctane, and benzene, the positions of the LF transition $\bar{\nu}_{5\%}$ are estimated to be $(22.6 \pm 0.4) \times 10^3$ cm^{-1}. From these electronic spectra the positions of the MLCT transitions are estimated to be at $(19.5 \pm 0.4) \times 10^3$ cm^{-1} and $(18.5 \pm 0.4) \times 10^3$ cm^{-1}.

Luminescence Data. Luminescence with quantum yields of the order of 10^{-4}–10^{-3} was observed from $W(CO)_5L$ complexes, where L is 4-ACpy, 4-BNpy, 4-CNpy, and 4-FMpy following excitation in fluid solution (see Figure 2 and Table II). These results are the first of their kind obtained from group 6B metal carbonyl complexes. Very weak emissions with decays which were immeasurable on our apparatus were observed from other $W(CO)_5L$ complexes in fluid solution, where L = pyridine, piperidine, diethylmethylamine, triethylamine, 2,4,6-trimethylpyridine, 2-acetylpyridine, 2-benzoylpyridine, acetone, diethyl ether, ethanol, and 1-pentene. The more electron-withdrawing substituents give rise to lower-energy MLCT excited states; when the ligand substituent is the acetyl, benzoyl, cyano, or formyl groups and in the para position on the pyridine, the MLCT excited states move below the LF excited state. The $W(CO)_5L$ complexes which have MLCT excited states as the lowest-energy absorption features (see Figure 1, Table I, and ref 51) exhibit measurable luminescence and relatively long radiative decays in fluid solution. These observations support those made previously for $W(CO)_5L$ complexes in EPA glasses.[51]

Solvent effects for the $W(CO)_5L$ luminescence are also noticeable. For the nonpolar solvents studied, the emissions were generally of greater yield and with longer lifetime compared to the more polar solvents. For the $W(CO)_5L$ complexes in tetrahydrofuran and ethanol, the luminescence was very weak and the emission lifetimes were relatively short. These effects are attributed to an increased rate of nonradiative decay from the excited state of $W(CO)_5L$ in the more polar solvents. As a result of thermal substitution reactions of the $W(CO)_5L$ complexes in tetrahydrofuran and ethanol, lifetime data were not obtained for temperatures above 283 K.

The pattern for our $W(CO)_5L$ series is that if the MLCT absorptions lie below the first ligand field absorption, emission of relatively long lifetime is observed. As a caution against generalization, the complex $W(CO)_5$(benzo[*c*]cinnoline) showed no detectable emission, yet has a MLCT absorption at 538 nm in *n*-hexane solvent,[55] or well below the energy of such absorptions in our series. The benzo[*c*]cinnoline ligand is presumably coordinated through one of the nitrogen atoms.[55] It is not clear why this complex behaves differently from those of our series, but it may be relevant that the 538-nm MLCT band does not show a long wavelength shoulder, while our series of complexes do.



The energy of an emitting state can be approximated from the short wavelength tail of the emission spectrum. We have assumed the emission band from a $W(CO)_5L$ complex to be gaussian, and have taken the $\bar{\nu}_{0-0}$ transition to be $\bar{\nu}_{5\%}$, where emission intensity at $\bar{\nu}_{5\%}$ = (0.05)(emission intensity at $\bar{\nu}_{max}$). The positions of the emitting state ($\bar{\nu}_{5\%}$) for the $W(CO)_5L$ complexes, where L = 4-ACpy, 4-BNpy, 4-CNpy, and 4-FMpy in methylcyclohexane and benzene, were thus estimated from the emission spectra of Figure 2 to be $(19.6 \pm 0.4) \times 10^3$ cm^{-1} in each case. This value is equal within experimental error to the $\bar{\nu}_{0-0}$ of the higher-energy MLCT absorption; the emission is therefore assigned to this transition for each of the $W(CO)_5L$ complexes. The MLCT excited state which was estimated to have an energy of $(18.5 \pm 0.4) \times 10^3$ cm^{-1} has too low an energy to be the emitting state.

The luminescence data that were obtained from the $W(CO)_5L$ complexes in solution were observed to be the same following either 353- or 530-nm excitation pulses. The pulse excitation energy of 530 nm corresponds to 18.9×10^3 cm^{-1}, too low to populate the MLCT excited state at $(19.6 \pm 0.4) \times 10^3$ cm^{-1}. It is assumed that thermal energy is required from the solution to populate this state. However, at glass temperatures very little energy will be available to the excited $W(CO)_5L$ molecule from its environment and excitation at 530 nm should not produce the emitting state. This we confirmed by experiment; $W(CO)_5$(4-CNpy) in a methylcyclohexane glass at 77 K was observed to luminesce following 353-nm excitation, but no luminescence was observed following 530-nm excitation. This is further evidence that it is the higher-energy MLCT excited state that is the emitting state.

The apparent activation energy for the emission intensity of $W(CO)_5$(4-ACpy) in methylcyclohexane is 2.4 ± 1 kcal mol^{-1}, and equal to the mean of the apparent activation energies obtained from the temperature dependence of the emission lifetimes for the $W(CO)_5L$ complexes in solution (Table IV). This activation energy, within experimental error, corresponds to the energy differences assigned between the low-lying MLCT excited states. Furthermore, the emission intensity increases and the emission lifetime decreases as the solution temperature is raised, behavior which is uncharacteristic of a single emitting state. These results imply that the higher-energy MLCT excited state (the emitting one) is thermally populated by the lower-energy MLCT excited state for the $W(CO)_5L$ complexes which luminesce in fluid solution.

Quenching experiments were undertaken to bracket the energies of the excited states of $W(CO)_5L$, where L = 4-ACpy, 4-BNpy, 4-CNpy and 4-FMpy. These $W(CO)_5L$ complexes were observed to act as quenchers at approximately diffusion-controlled rates for the phosphorescence of benzophenone and biacetyl. The triplet energies (E_T) for benzophenone and biacetyl are 24.0×10^3 and 19.2×10^3 cm^{-1}, respectively.[63] Assuming that the quenching process is energy transfer, this places the energy of the quenching excited state of $W(CO)_5L$ as $\leq 19.2 \times 10^3$ cm^{-1}. Also, the $W(CO)_5L$ emission was quenched by several anthracenes, which strongly suggests that energy transfer is the quenching mechanism.

---

(62) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6874–6876.

(63) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley-Interscience: New York, 1966; p 298.

Table V. Solvent and Temperature Dependence of Photosubstitution Quantum Yields for 5–7 × 10^{-5} M $W(CO)_5$(4-CNpy) in Solutions Containing 0.05 M Ethanol (Irradiation Wavelength = 465 nm)

	quantum yield with the following solvents				
temp, K	methyl-cyclohexane	iso-octane	benzene	THF	ethanol
283	0.030	0.030	0.030	0.030	0.029
288	0.038	0.037	0.044		
293	0.048	0.048	0.053		
298	0.062	0.063	0.061		
303	0.074	0.072	0.078		

As previously noted, $W(CO)_5L$ emissions were quenched by anthracene (E_T = 14.7 × 10^3 cm^{-1}),[64] 9-methylanthracene (E_T = 16.2 × 10^3 cm^{-1}),[64] 1,2-benzanthracene (E_T = 16.5 × 10^3 cm^{-1})[64] and acenaphthaquinone (E_T = 17.9 × 10^3 cm^{-1}),[65] but not by 1,2,5,6-dibenzanthracene (E_T = 18.3 × 10^3 cm^{-1}),[64] fluoranthene (E_T = 18.5 × 10^3 cm^{-1}),[64] benzil (E_T = 18.8 × 10^3 cm^{-1}),[63] coronene (E_T = 19.1 × 10^3 cm^{-1}),[64] or chrysene (E_T = 20.0 × 10^3 cm^{-1}).[64] These results bracket the energy of the quenchable excited state of $W(CO)_5L$ to be (17.9 × 10^3)–(18.3 × 10^3) cm^{-1}. The data imply that it is only the lower-energy MLCT excited state ((18.5 ± 0.4) × 10^3 cm^{-1}) that is involved in the energy-transfer mechanism.

The quenching of the emission lifetime of $W(CO)_5$(4-CNpy) follows Stern–Volmer kinetics (Figure 3) with a bimolecular quenching rate constant approaching that of the diffusion-controlled limit.

Photosubstitution Reactivity. Photodissociation of the ligand (L) has been shown to be the most efficient chemical process over our excitation region (eq 6).[15,51,57] In the presence of an excess

$$W(CO)_5L \xrightarrow[C_2H_5OH]{h\nu} W(CO)_5(C_2H_5OH) \qquad (6)$$

of entering ligand, e.g., 0.025–0.1 M ethanol, the photosubstitution reaction appears to be uncomplicated by side or subsequent reactions. Figure 4 illustrates the spectral sequence accompanying the 465-nm photolyses of $W(CO)_5L$ complexes, showing a clear progression to near zero terminal absorbance in the 450–500-nm region. The quantum yields, ϕ, determined for reaction 6 are listed in Table V. The low values are consistent with results reported for substituted pyridine ligands of this type;[51] this seems to be characteristic of the case where the MLCT state lies below the LF state. Quantum yields for complexes in which the LF state is lowest in energy are significantly higher.[51]

The quantum yield for $W(CO)_5$(4-CNpy) undergoing reaction 6 does not show a solvent dependence. In tetrahydrofuran and ethanol, the quantum yields for $W(CO)_5$(4-CNpy) were measured at 283 K only, since thermal substitution reactions were taking place at higher temperatures. The lack of dependence of the quantum yield on ethanol concentration is a good indication that ethanol is not a quencher in solution and does scavenge completely the photochemically produced $W(CO)_5$ intermediate.

As noted under Results, quantum yields for $W(CO)_5$(4-CNpy) are temperature dependent. The apparent activation energies for the photosubstitution quantum yields at 465 nm of $W(CO)_5$(4-CNpy), in methylcyclohexane, isooctane, and benzene are the same within experimental error, with a mean value of 7.8 ± 1 kcal mol^{-1}. Quantum yields for $W(CO)_5$(4-ACpyr) and $W(CO)_5$(4-BNpyr) were lower than the above ones at any given temperature, the data corresponding to apparent activation energies of 7.9 ± 1 and 7.5 ± 1 kcal mol^{-1}, respectively. These activation energies correspond, within experimental error, to the energy difference between the higher-energy MLCT state ((19.6 ± 0.4) × 10^3 cm^{-1}) and the LF state ((22.6 ± 0.4) × 10^3 cm^{-1}); the implication is that chemical reaction occurs from the higher-lying LF state, which is in thermal equilibrium[66] with the emitting CT state. The quantum yield for $W(CO)_5$(4-CNpy) in methylcyclohexane is dependent on the irradiation wavelength, being larger following higher energy excitation. The apparent activation energy following 520-nm photolysis (7.6 ± 1 kcal mol^{-1}) is the same within experimental error as that observed for the 465-nm photolysis (7.9 ± 1 kcal mol^{-1}), whereas the apparent activation energy following 430-nm photolysis (3.2 ± 1 kcal mol^{-1}) is significantly lower. We attribute these observations to direct population of the LF excited state following 430-nm excitation, which gives rise to substitution at a competitive rate to internal conversion to the relatively unreactive low-lying MLCT states.

The quenching of the photosubstitution quantum yield of $W(CO)_5$(4-CNpy) by anthracene at 520 nm follows Stern–Volmer kinetics, with a slope common within experimental error to that observed for the emission lifetime quenching (Figure 3). This result strongly indicates that the emitting state of $W(CO)_5$(4-CNpy) is implicated in the photochemistry. Quantum-yield quenching measurements are also recorded with 430-nm excitation. The data do not obey Stern–Volmer kinetics (see Figure 3). The nonlinear behavior is further evidence of direct population of the LF excited state following 430-nm excitation, which chemically reacts at a rate competitive to internal conversion to the quenchable low-lying MLCT states.

Whereas the quantum yield (ϕ) quenching data for $W(CO)_5$(4-CNpy) in methylcyclohexane are dependent on the excitation wavelength, the emission lifetime (τ) quenching data can be assumed to obey the measured Stern–Volmer type kinetics at any excitation wavelength. The extent of unquenchable photolysis at 430 nm of $W(CO)_5$(4-CNpy) in methylcyclohexane is obtainable by plotting ϕ/ϕ^0 vs. τ/τ^0.[67] The plot is linear, with intercept 0.33, so that the yield is 33% unquenchable. We attribute this unquenchable yield to direct chemical reaction through the LF excited state following 430-nm excitation of $W(CO)_5$(4-CNpy) in methylcyclohexane.

Excited-State Absorption and Primary Photoproduct Spectra. The excited-state absorption (ESA) spectra for $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), and $W(CO)_5$(4-CNpy) in methylcyclohexane and benzene show two absorption features (Figure 5). These decay with the lifetime of the emitting state. We therefore assign the ESA absorption features to be due to transitions from the higher-energy MLCT state to high-energy excited states. If two low-lying MLCT states are in fact present, the ESA we observe could actually be a mixed absorption spectrum.

The absorption spectra of the primary photoproducts of $W(CO)_5$(4-ACpy), $W(CO)_5$(4-BNpy), and $W(CO)_5$(4-CNpy) following laser pulse photolysis are coincident within experimental error in methylcyclohexane (λ_{max} = 428 nm) and benzene (λ_{max} = 402 nm) (see Figure 6). For the $W(CO)_5L$ complexes in methylcyclohexane, the value of ϵ_{max} is 6.7 × 10^3 M^{-1} cm^{-1}, and the position of the maximum is within the range of wavelengths reported for tungsten pentacarbonyl species generated in low-temperature SF_6 (461 nm), Ar (437 nm), Xe (417 nm), and CH_4 (413 nm) matrices,[13] as well as in the pulsed-radiolysis study in cyclohexane (415 nm).[68] Recently, we have shown that the intermediate produced in the laser pulse photolysis of $W(CO)_6$ in methylcyclohexane at room temperature is a solvent-coordinated species, $W(CO)_5S$, which is then scavenged by the entering ligand.[27] The absorption spectrum of this intermediate is the same within experimental error as that shown here, which implies that the common primary photoproduct of the $W(CO)_5L$ complexes is the $W(CO)_5S$ species.

Summary

Our results have shown that the emitting state of the $W(CO)_5L$ complexes is implicated in the photochemistry, that is, chemical

---

(64) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; p 182.

(65) Fang, T-S.; Singer, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 6276–6278.

(66) The two states would be in true thermal *equilibrium* only if all other rates by which they appear and disappear are negligible compared to the LF $\rightleftharpoons$ CT forward and reverse rates. The expression "steady-state thermal equilibrium" might be more appropriate.

(67) Ballardini, R.; Varani, G.; Wasgestian, H. F.; Moggi. L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2947–2951.

(68) Flamigni, L. *Radiat. Phys. Chem.* **1979**, *13*, 133–138.

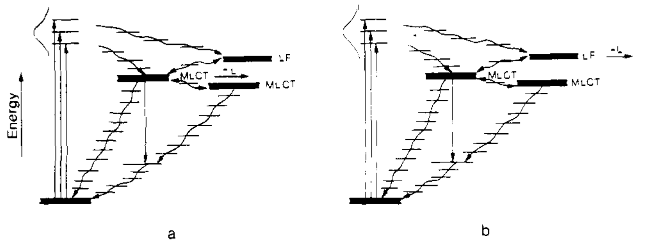


Figure 7. Energy vs. distortion diagrams for W(CO)$_5$L. Heavy horizontal lines represent thexi (thermally equilibrated excited) states. Light horizontal lines represent successive complex–solvent cage energies as a vibrationally excited state relaxes to its thexi state (only a few of the lines are shown). Heavy vertical lines denote radiative processes and wavy lines denote nonradiative processes.

reaction occurs from or via this state. Two low-lying MLCT excited states are inferred, the emitting one at $(19.6 \pm 0.4) \times 10^3$ cm^{-1} and one which is quenchable at $(18.5 \pm 0.4) \times 10^3$ cm^{-1}. A LF excited state at $(22.6 \pm 0.4) \times 10^3$ cm^{-1} has been estimated from the electronic absorption spectra. Possible excited-state schemes for the W(CO)$_5$L complexes which luminesce in fluid solution are shown in Figure 7.

Scheme a in Figure 7 shows the reactive state to be the lowest-lying MLCT state. The photochemical reaction presumably occurs by dissociation of the W–L bond to form a W(CO)$_5$ or W(CO)$_5$S intermediate, which is then scavenged by the entering ligand. The W–L bond-breaking reaction must then be activated to the extent of 7.6 ± 1 kcal mol^{-1}.

Scheme b in Figure 7 presents an attractive alternative, in which chemical reaction occurs from the LF state lying above the low-lying MLCT states and in steady-state equilibrium with them. The observed activation energy for the photosubstitution reaction is now attributed primarily to the energy difference between the LF and MLCT states. In this scheme, excitation leads, through the intersystem crossing, to a MLCT state. This state is emitting but not highly chemically reactive. The higher-energy LF state does react efficiently, but the overall quantum yield is small because of the competition with nonradiative decay at the MLCT state. The detailed kinetics for such a system have been reported elsewhere.[69-71] At higher excitation energies, the LF state is directly populated, and as a consequence, the quantum yields for photosubstitution are increased. Similarly, at higher excitation energy the W(CO)$_5$L photosubstitution shows a significantly lower temperature dependence and the quenching data do not obey Stern–Volmer kinetics. This type of scheme, b in Figure 7, has been proposed to explain the photochemical behavior of Ru(NH$_3$)$_5$L^{2+} complexes[33] as well as that for the present type of carbonyl complexes.[56,72] It has the appealing feature of accounting for the increase in the quantum yield for photosubstitution for W(CO)$_5$L complexes, where L is such that the MLCT absorption bands are at higher energy than the LF one.

Experimental Section

Materials. Tungsten hexacarbonyl (Strem Chemicals) was purified by sublimation. The ligands pyridine, piperidine, diethylmethylamine, triethylamine, 2,4,6-trimethylpyridine, acetone, diethyl ether, and ethanol are commercially available and were distilled prior to use. The ligands 1-pentene (Tridom Chemical), 2-acetylpyridine, 4-acetylpyridine, 2-benzoylpyridine, 4-benzoylpyridine, 4-cyanopyridine, and 4-formylpyridine (Aldrich) were used without further purification. Chemicals used in quenching experiments were obtained from Aldrich and purified as follows: anthracene (recrystallized from benzene), acenaphthaquinone (recrystallized from ethanol), 1,2-benzanthracene (resublimed), benzil (resublimed), benzophenone (recrystallized five times from ethanol), biacetyl (distilled twice), 9-methylanthracene and 1,2,5,6-dibenzanthracene (recrystallized from benzene); coronene, chrysene, and fluoranthene were used without further purification. Solvents used were obtained from MCB Manufacturing Chemists and were OmniSolv grade. The methylcyclohexane, tetrahydrofuran (THF), and ethanol, however, were further purified by several distillations, so as to remove emitting impurities. Alumina (MCB Manufacturing Chemists) and silica gel (Matheson, Coleman and Bell) were used as chromatographic sorbents.

Synthesis of W(CO)$_5$L. W(CO)$_5$L complexes were prepared in solution by 313-nm photolysis of 10^{-4} M W(CO)$_6$ and 0.1 M L in argon purged methylcyclohexane (reaction 1). W(CO)$_5$L complexes were prepared and isolated by reacting 4 mmol of photoproduced W(CO)$_5$(THF) with 4 mmol of L in argon-purged THF (reactions 2 and 3). The THF was removed by rotary evaporation and the solid product was redissolved in isooctane and purified by column chromatography on alumina or silica gel. The main impurities were found to be unreacted W(CO)$_6$ and L. Elution first was with isooctane until the UV absorption features of W(CO)$_6$ could no longer be detected in the eluant, followed by elution of the product complex with benzene or toluene. The product was recovered by rotary evaporation and further purified by recrystallization. The infrared and UV-vis absorption spectra agreed well with those published.[51] Chromatographic adsorbents, elution agents, crystallization solvents, and elemental analyses are given below.

W(CO)$_5$(pyridine): alumina, benzene, isooctane–benzene. Anal. Calcd: C, 29.8; H, 1.3; N, 3.5. Found: C, 30.1; H, 1.4; N, 3.3.

W(CO)$_5$(piperidine): alumina, benzene, isooctane–benzene. Anal. Calcd: C, 29.4; H, 2.7; N, 3.4. Found: C, 29.0; H. 2.7; N, 3.7.

W(CO)$_5$(4-acetylpyridine): alumina, benzene, *n*-hexane–benzene. Anal. Calcd: C, 32.4; H, 1.6; N, 3.1. Found: C, 32.9; H, 1.8; N, 3.3.

W(CO)$_5$(4-benzoylpyridine): alumina, benzene. *n*-hexane–benzene. Anal. Calcd: C, 40.3; H, 1.8; N, 2.8. Found: C, 41.0; H, 1.9; N, 2.8.

W(CO)$_5$(4-cyanopyridine): alumina, benzene isooctane–toluene. Anal. Calcd: C, 30.9; H, 0.9; N, 6.5. Found: C, 30.3; H, 1.0; N, 6.8.

W(CO)$_5$(4-formylpyridine): silica gel, benzene–isooctane (1:2), isooctane–benzene. Anal. Calcd: C. 30.7, H, 1.2; N, 3.3. Found: C, 30.0; H, 1.1; N, 3.5.

Equipment and Procedures. Details of the laser photolysis and monitoring equipment are described elsewhere.[73,74] Emission lifetimes were recorded using either frequency doubled (530 nm) or tripled (353 nm) 20-ns pulses from the Nd glass laser and considered to be accurate to ±10%. Emission was recorded at any single wavelength (in 600–650-nm region) by a Jarrell-Ash Mark 10 monochromator and detected by an RCA 7265 photomultiplier and Tektronix Model 7844 oscilloscope. Corning glass filters were placed on the monochromator entrance slit to block out the laser light but transmit at greater than 580 nm. Plots of log (emission intensity) vs. time were linear for all complexes from which luminescence was recorded. Excitation was at 353 nm for monitoring experiments. For these experiments, the 1-cm diameter laser beam was shaped by using a cylindrical lens to give an irradiated area of 2 × 9 mm on the front window of a four clear-sided cell. The monitoring beam traversed the full 1-cm width of the irradiation cell, but the excitation pulse was shaped to be 9-mm wide. Thus the monitoring beam passes through 1 mm of unphotolyzed solution and 9 mm of photolyzed solution. The transmitted monitoring beam was reduced onto the slit of the monochromator and excited onto a five-stage RCA 4840 photomultiplier. Saturation effects were avoided by employing a mechanical shutter. Typical entrance and exit slits in either experiment were 1 mm.

Emission spectra at 298 K were recorded with a Perkin-Elmer Model 650-10S fluorescence spectrophotometer and corrected for the Hamamatsu R928 photomultiplier. Emission spectra at 77 K were recorded with the Nd glass laser. Luminescence quantum yields were calculated with use of a known emitter, Ru(bipy)$_3{}^{2+}$.[40]

Photolysis experiments were performed with an Illumination Industries 200-W medium-pressure mercury arc lamp. Rolyn Optics Co. and Baird-Atomic interference filters (10-nm band-pass) were used to isolate irradiation wavelengths at 430, 465, and 520 nm. Typical light intensities were 10^{-8}–10^{-7} Einstein s^{-1}, determined by Ferrioxalate[75] (430 nm) or Reineckate[76] (465 and 520 nm) actinometry. Quantum yield measurements were made for disappearance of starting material in the 450–500-nm region. They were corrected for the small inner filter effects due to product formation and changing degree of light absorption when

---

(69) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614.

(70) Porter, G. B. "Concepts of Inorganic Photochemistry"; Adamson, A. W.; Fleischauer, P. F., Eds.; Wiley-Interscience: New York, 1975; pp 37–79.

(71) Kane-Maguire, N. A. P.; Toney, C. G.; Swiger, B.; Adamson, A. W.; Wright, R. E. *Inorg. Chim. Acta* **1977**, *22*, L11–L13.

(72) See ref in 16 and 51; also Wrighton, M. S., private communication.

(73) Gutierrez, A. R.; Adamson, A. W. *J. Phys. Chem.* **1978**, *82*, 902–907.

(74) Fukuda, R.; Walters, R. T.; Macke, H.; Adamson, A. W. *J. Phys. Chem.* **1979**, *83*, 2097–2103.

(75) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A.* **1956**, *235*, 518–536.

(76) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394–404.

necessary. Reproducibility was within ±10%.

In the emission, monitoring, and photolysis experiments, sample solutions were filtered immediately before use through a 0.22-μm Millipore filter and transferred to a 1 × 1-cm spectrofluorimeter cell. The solutions were deaerated by argon purging for 20 min. The temperature of the solution in the cell was controlled to 0.1 °C by circulating thermostated water.

Luminescence data of solid W(CO)$_5$L were recorded with use of a triangular cell with the front face at 45° to the exciting light. Conventional absorption spectra were obtained by means of Cary Model 14R and Hewlett-Packard 8450A recording spectrophotometers. Infrared spectra were recorded in isooctane with a Perkin-Elmer Model 281 spectrometer.

Elemental analyses were performed by Analytical Facility, California Institute of Technology.

Acknowledgment. We wish to thank Professor H. Kisch for the sample of W(CO)$_5$ (benzo[*c*]cinnoline). This investigation was supported in part by a contract with the U.S. Office of Naval Research.

Registry No. W(CO)$_5$(pyridine), 14586-49-3; W(CO)$_5$(piperidine), 31082-68-5; W(CO)$_5$(4-acetylpyridine), 60166-30-5; W(CO)$_5$(4-benzoylpyridine), 60166-31-6; W(CO)$_5$(4-cyanopyridine), 60166-32-7; W(CO)$_5$(4-formylpyridine), 60166-33-8; W(CO)$_6$, 14040-11-0; W(CO)$_5$(THF), 36477-75-5.

Excitation Energies in Trimethylenemethane Derivatives

Sheila B. Auster, Russell M. Pitzer,* and Matthew S. Platz

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received October 7, 1981*

Abstract: Calculations of triplet-to-singlet and other excitation energies have been carried out on two derivatives of trimethylenemethane (TMM), I modified to contain a five-membered ring and II also including two methyl groups, using (9s5p/4s), [4s3p/2s] Gaussian basis sets. The triplet–singlet energy for II is computed to be 11.7 kcal/mol, only 3.2 kcal/mol lower than that of TMM itself. Additional calculations were carried out in order to make comparisons and as an aid in understanding the effects of the substituents, with results consistent with previous ideas and models of radical stabilization.

Trimethylenemethane (TMM) and its derivatives have been studied for several reasons. In 1948 it was pointed out that the central carbon atom in TMM (unsynthesized at that time) has the highest bond order possible for a trigonal carbon atom,[1] and thus TMM is a benchmark in Coulson's free valence system.[2] The nonclassical bonding of TMM, its predicted triplet ground state, and its small size add to its theoretical interest and have made it a common textbook example in discussions of molecular orbital (MO) theory.[3,4] Published theoretical studies of TMM have run the gamut from qualitative MO treatments[5] to extensive calculations with configuration interaction wave functions.[6,7]

TMM and TMM derivatives have been postulated as intermediates in a number of reactions involving methylenecyclopropanes[8-10] in which the mechanism required a low-lying singlet state with a low barrier to rotation about the methylene–ring bond. No direct observations of TMM were made, however, until Dowd[11] reported its synthesis and ESR spectrum in 1966. Subsequently there has been a considerable amount of further work on TMM,[12,13] complexes of Fe(CO)$_3$ and TMM derivatives,[14-16] and reactions of methylenecyclopropanes.[17]

Perhaps the most interesting question regarding TMM and its derivatives at present concerns the excitation energy from the ground (triplet) state to the excited (singlet) state. The best theoretical calculation to date of the energy difference from the lowest energy ground-state geometry (planar D_{3h} $^3A_2'$) to the lowest energy excited-state geometry (nonplanar C_{2v} $^1B_1$) is 14 kcal/mol.[7] The experimental measurement that is available for comparison is the activation energy for the disappearance of the TMM ESR spectrum, 7.0 kcal/mol.[18] It is not entirely clear how this value is related to the excitation energy.[19,20] For the alkyl-substituted TMM (II), however, a 3.5 kcal/mol value for the upper limit of the excitation energy has been obtained[21] by the analysis of kinetic data from matrix olefin condensation reactions. Since the comparison of the 14 kcal/mol and 3.5 kcal/mol values is hampered by the fact that they are obtained for different molecules, we felt that it was important to calculate the excitation energy for the TMM derivatitive (II) itself.

---

(1) C. A. Coulson, *J. Chim. Phys. Phys.-chim. Biol.*, **45**, 243 (1948).

(2) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952).

(3) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961.

(4) L. Salem, "Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966.

(5) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

(6) D. M. Hood, R. M. Pitzer, H. F. Schaefer III, *J. Am. Chem. Soc.*, **100**, 2227 (1978).

(7) D. M. Hood, R. M. Pitzer, H. F. Schaefer III, *J. Am. Chem. Soc.*, **100**, 8009 (1978).

(8) E. F. Ullman, *J. Am. Chem. Soc.*, **82**, 505 (1960).

(9) J. J. Gajewski, *J. Am. Chem. Soc.*, **93**, 4450 (1971).

(10) W. von E. Doering and L. Birlandeanu, *Tetrahedron*, **29**, 499 (1973).

(11) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).

(12) P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967).

(13) P. Dowd, A. Gold, and K. Sachdev, *J. Am. Chem. Soc.*, **90**, 2715 (1968).

(14) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **88**, 3172 (1966).

(15) A. Almenningen, A. Haaland, and K. Wahl, *J. Chem. Soc., Chem. Commun.*, 1027 (1968).

(16) M. R. Churchill and K. Gold, *J. Chem. Soc., Chem. Commun.*, 693 (1968).

(17) P. Dowd, G. Sengupta, and K. Sachev, *J. Am. Chem. Soc.*, **92**, 5726 (1970).

(18) P. Dowd and M. Chow, *J. Am. Chem. Soc.*, **99**, 6438 (1977).

(19) J. A. Berson, *Acc. Chem. Res.*, **11**, 446 (1978).

(20) Aside from the intrinsic difficulties in precise comparisons of activation energies with energy surface features, Berson (ref 19) and Davidson and T. Borden (as quoted in ref 7) have suggested that the activation energy in this case may correspond to a surface crossing rather than an excitation energy. Unpublished calculations by E. R. Davidson, K. Tanaka, and W. T. Borden have not, however, shown such a low-energy crossing.

(21) M. S. Platz and J. A. Berson, *J. Am. Chem. Soc.*, **99**, 5178 (1977). Further experiments have demonstrated that an appreciable concentration of the then unknown bicyclic species III was present in the matrix experiment. Since the ultimate fate of III in the presence of olefins is the formation of the same adducts that derive from the singlet biradical, the apparent excitation energy of 3.5 kcal/mol, which was obtained previously, is too low. See M. Rule, M. G. Lazzara, and J. A. Berson, *J. Am. Chem. Soc.*, **101**, 7091 (1979). Recent work indicates that the lowest-lying planar singlet biradical (II) is at least 13 kcal/mol above the ground-state triplet, which is consistent with the calculations presented here ($^1B_2$ = 16.3 kcal/mol and $^1A_1$ = 15.4 kcal/mol when the correction discussed in the text is included). The energy separation between the lowest lying orthogonal singlet ($^1B_1$) and the ground-state triplet has not been determined experimentally. See M. R. Mazur and J. A. Berson, *J. Am. Chem. Soc.*, **103**, 684 (1981), and J. A. Berson in "Diradicals", W. T. Borden, ed., Wiley, New York, in press.

0002-7863/82/1504-3812$01.25/0