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PHOTOCHEMISTRY OF *cis*-TETRACARBONYLBIS(*trans*-4-STYRYLPYRIDINE)TUNGSTEN(0): INTRALIGAND PHOTOISOMERIZATION FROM UPPER EXCITED STATES

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Summary

The excited state reactivity and electronic absorption spectrum of *cis*-tetracarbonylbis(*trans*-4-styrylpyridine)tungsten have been investigated. The lowest excited state in absorption is predominantly W→*trans*-4-styrylpyridine charge transfer (CT) in character. An absorption band near 465 nm ($\epsilon \approx 10\,000$ l mol^{-1} cm^{-1}) in benzene is associated with this transition, and this band shifts to the blue in more polar or polarizable media in a manner comparable to other M→ ligand CT absorptions in metal carbonyls. Ligand field transitions can be observed in the vicinity of 400 nm, but the near-UV spectrum is dominated by intense intraligand, IL, $\pi \rightarrow \pi^*$ *trans*-4-styrylpyridine absorption. The photochemistry involves *trans*→*cis* isomerization of the coordinated ligand, but the wavelength dependence of the quantum yields indicates upper excited state reaction; the $\pi \rightarrow \pi^*$ IL is concluded to be responsible for the isomerization. The lowest excited CT state undergoes little or no photosubstitution or ligand isomerization. The *trans*→*cis* ligand isomerization quantum yield is <0.001 at 436 nm, but is ~0.10 at 313 nm indicating relatively slow internal conversion from the IL to the CT state compared to *trans*→*cis* ligand reaction.

In recent years there have been several reports of what appears to be intraligand photochemistry in metal complexes. Irradiation of azide complexes has been found to yield coordinated nitrene [1,2]; simple alkenes undergo cycloaddition upon irradiation of alkenecopper(I) complexes [3,4]; and an interesting metal photoassisted ring closure was used in the synthesis of vitamin B_{12} [5]. These three examples demonstrate in some measure the potential importance of stoichiometric use of photons in metal complex photoassisted processes. In all

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cases where intraligand photochemistry is possible other competing processes can occur, including both non-chemical and chemical nonradiative decay channels. For example, if internal conversion from some intraligand (IL) excited state achieved by direct irradiation completely efficiently relaxes to a lower state which only gives substitution, then any expected IL reaction may not occur. Thus, it is important to build up information concerning the control of competitive excited state processes.

The aim of this paper is to report the results of an investigation of the excited state behavior of *cis*-tetracarbonylbis(*trans*-4-styrylpyridine)tungsten, (*cis*-$W(CO)_4(t\text{-}4)_2$). Styrylpyridine itself has been well studied with respect to its excited state behavior [6—8]. Other studies of the photochemistry of styrylpyridine complexes have also been reported. These include (i) investigation [9] of pentacarbonylstyrylpyridinetungsten where a ligand field (LF) state is the lowest excited state observable in the absorption spectrum; (ii) study [10] of tricarbonylhalobis(styrylpyridine)rhenium where the lowest excited state in absorption is $\pi \to \pi^*$ styrylpyridine IL in character and (iii) reports [11] on the photochemistry of styrylpyridineruthenium(II) complexes having lowest ruthenium(II)→ligand charge transfer (CT) excited states.

Results and discussion

a. Electronic spectral studies

We have attempted to observe luminescence from *cis*-$W(CO)_4(t\text{-}4)_2$, but under no conditions (pure solid or degassed solutions at 298 or 77 K) have we been able to detect optical emission. While we are reluctant to say that any substance is totally non-luminescent, we can state that the emission is non-detectable under conditions where emission from substances like $W(CO)_4$(1,10-phenanthroline) is easily detectable [12]. The comparison is appropriate since the 1,10-phenanthroline and bis(*trans*-4-styrylpyridine) complexes have similar visible absorption spectral properties with a common assignment for the observed bands, vide infra.

The 298 and 77 K electronic absorption spectra of *cis*-$W(CO)_4(t\text{-}4)_2$ in EPA are shown in Fig. 1, and 298 K band positions and intensities are given in Table 1 for several solvents. The absorption spectrum of the complex consists of an intense, $\epsilon \approx 50\,000$ l mol^{-1} cm^{-1} UV maximum near 310 nm and a series of lower intensity bands in the lower energy UV and visible region.

1. IL band. The band maximizing in the UV at ~310 nm is very clearly the IL $\pi \to \pi^*$ styrylpyridine transition. We draw this conclusion from the intensity and the vibrational structure. The value of ϵ for the *trans*-4-styrylpyridine in CH_2Cl_2 is ~28 000 l mol^{-1} cm^{-1} [10]. The value of ~50 000 l mol^{-1} cm^{-1} for the 310 nm band of the bis(styrylpyridine) complex is reasonable, since two IL chromophores are coordinated to the metal. The vibrational structure at 77 K on the band at ~310 nm also resembles the free ligand spectrum [10]. However, the first well defined vibrational maximum is at 352 nm for the complex and at 332 nm for the free ligand under the same conditions.

The IL band in *cis*-$W(CO)_4(t\text{-}4)_2$ is somewhat different in appearance (shape) and position compared to the IL band in $XRe(CO)_3(t\text{-}4)_2$ (X = Cl, Br) [10]. Specific differences are that (i) the Re complex exhibits a 298 K solution maximum at 330 nm vs. 310 nm for the W species reported here, and (ii) the Re com-

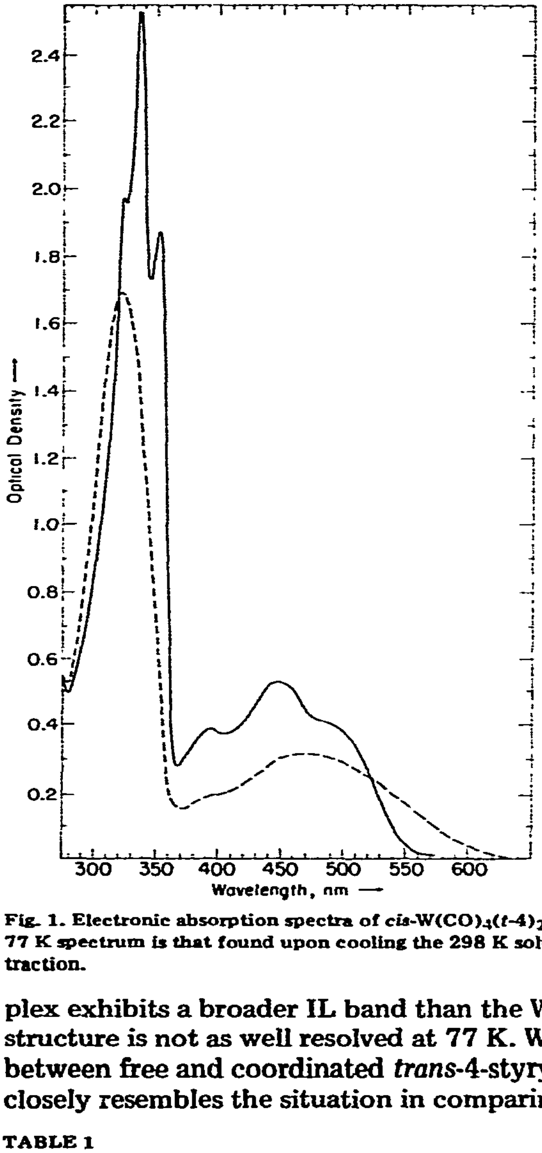


Fig. 1. Electronic absorption spectra of *cis*-W(CO)$_4$(*t*-4)$_2$ in EPA at 298 (- - - - - -) and 77 K (————). The 77 K spectrum is that found upon cooling the 298 K solution and has not been corrected for solvent contraction.

plex exhibits a broader IL band than the W complex, and for Re the vibrational structure is not as well resolved at 77 K. We concluded [10] that the comparison between free and coordinated *trans*-4-styrylpyridine in the Re complex very closely resembles the situation in comparing the free ligand and the protonated

TABLE 1

ELECTRONIC ABSORPTION SPECTRAL BAND MAXIMA FOR *cis*-TETRACARBONYLBIS(*trans*-4-STYRYLPYRIDINE)TUNGSTEN, (*cis*-W(CO)$_4$(*t*-4)$_2$)[a]

Solvent	Band maxima (nm)/ε (l mol^{-1} cm^{-1})	
Benzene	465/10 700;	310/44 200
CH_2Cl_2	437/10 500;	310/45 400
EPA	450/—;	308/—
CH_3CN/Benzene (90/10, V/V)	421/—;	308/—
Isooctane/benzene (70/30, V/V)	486/—;	308/—

[a] 25°C.

ligand. But for the *cis*-W(CO)$_4$(*t*-4)$_2$, the IL transition is apparently less perturbed by the coordination to W, and the IL band closely resemble the free ligand. Spectra of ClRe(CO)$_3$(*t*-4) and *trans*-4-styrylpyridine are reproduced in Fig. 2 for the purpose of comparison with the spectra in Fig. 1.

2. *W→4-styrylpyridine CT band.* Solvent effects on the lowest absorption band system in *cis*-W(CO)$_4$(*t*-4)$_2$ are quite substantial. Spectra at 298 K in two extremes of polar (or polarizable) and non-polar (or -polarizable) solvents are shown in Fig. 3. As expected, the IL transition is not much affected by solvent. The large blue-shift of the lowest energy band in the more polar or polarizable media is very consistent with what has been found for the W→1,10-phenanthroline CT band in W(CO)$_4$(1,10-phenanthroline) [12,13]. This solvent effect and the band position and intensity compared to W(CO)$_4$(ethylenediamine) [12,13] strongly support assignment of the lowest energy band system in *cis*-W(CO)$_4$(*t*-4)$_2$ as W→*t*-4 CT. In the 77 K spectrum shown in Fig. 1 the two components of the lowest energy band system at ~490 and 440 nm are associated with the CT transition. The W(CO)$_4$(1,10-phenanthroline) likewise exhibits a W→1,10-phenanthroline CT band having two resolved components at 77 K [12].

3. *LF band(s).* The LF spectra of *cis*-W(CO)$_4$bis(aliphatic amine) complexes have been reported previously [12,13], and invariably there is a band near 400 nm which is associated with the lowest spin-allowed LF transition. For *cis*-W(CO)$_4$(*t*-4)$_2$ a band appears at ~390 nm (cf. 77 K spectrum in Fig. 1) which we now assign as the lowest spin-allowed LF absorption. Obviously, not all of the absorbance at ~390 nm is due to the LF transition, since the CT band is broad. We simply take 390 nm as the approximate maximum of the LF band. A similar assignment was made for a band near 400 nm in W(CO)$_4$(1,10-phenanthroline) [12,13] and undergirding this assignment is the observation [14] that the LF bands in W(CO)$_5$(N-donor) are essentially independent of the N-donor, for a range of N-donors having no CT bands, to those yielding complexes having lowest or upper CT excited states (N-donor = piperidine, 3,4-dimethylpyridine, 4-formylpyridine). Preliminary observations in this laboratory support the general conclusion that the position of LF bands in *cis*-W(CO)$_4$(N-donor)$_2$ are also largely independent of the N-donor and whether there is a low lying CT band.

4. *Spin-forbidden absorption.* The absorption spectra of W(CO)$_6$ [15], W(CO)$_5$X [16], and W(CO)$_4$X$_2$ [12], have all been shown to exhibit relatively weak bands attributable to spin-forbidden, singlet→triplet, absorption. For *cis*-W(CO)$_4$bis(aliphatic amine) complexes the lowest LF singlet→triplet transition was associated with a shoulder at ~460 nm, and we note that this would fall in the region of the CT maximum in the complex of interest here. Additionally, on the basis of the presence of the third row transition element W we expect the lowest CT transition to have some singlet→triplet character as suggested for W(CO)$_4$(1,10-phenanthroline) [12]. We have been unable to detect any singlet→triplet IL absorption. A weak transition, perhaps intensified by the heavy metal atom, would be expected in the vicinity of ~580—600 nm, assuming that the triplet energy of ~50 kcal/mol [6] for the free ligand would not be significantly perturbed by coordination. This assumption is justified on the basis of the relatively non-perturbed IL singlet→singlet transition. Difficulty is encountered in attempting to observe the spin-forbidden IL band, since it likely falls on the tail of the intense CT band.

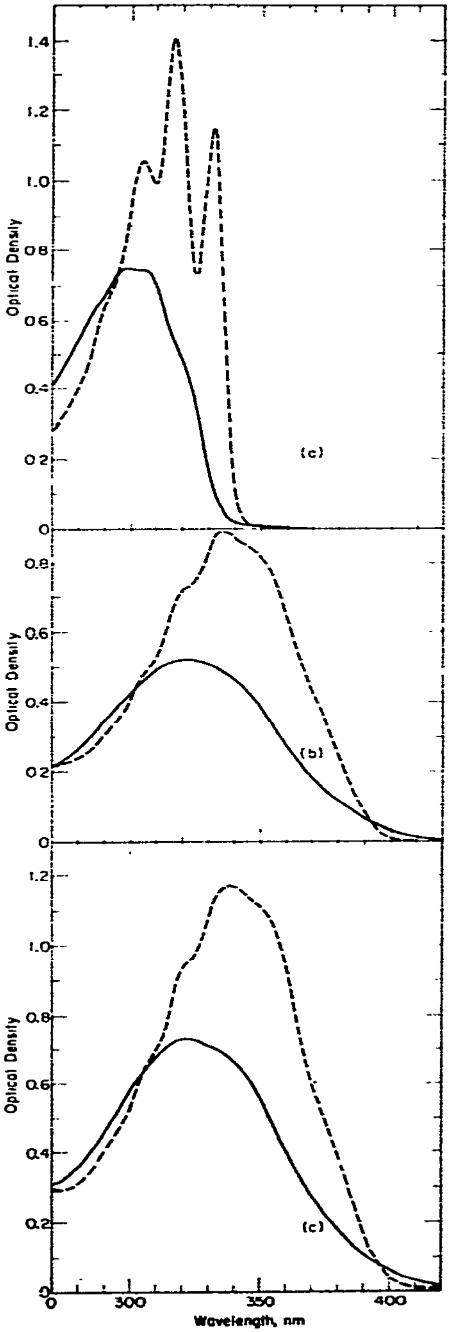


Fig. 2. Spectra of (a) *trans*-4-styrylpyridine, (b) ClRe(CO)$_3$(t-4)$_2$, and (c) BrRe(CO)$_3$(t-4)$_2$ in EPA at 298 (———) and 77 K (- - - - - -). The spectra at 77 K are obtained after cooling the 298 K solutions and have not been corrected for solvent contraction. The molar absorptivity at the band maxima are: (a) 28 000 M^{-1} cm^{-1}, (b) 50 300 M^{-1} cm^{-1}, (c) 53 200 M^{-1} cm^{-1}.

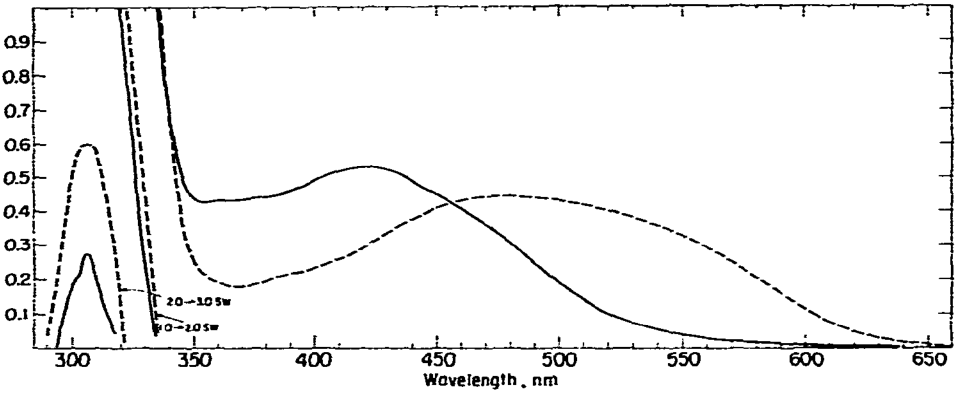


Fig. 3. Electronic spectra of *cis*-W(CO)$_4$(*t*-4)$_2$ at 298 K in isooctane/benzene (70/30 V/V) (- - - - - -) and CH$_3$CN/benzene (90/10 V/V) (———). Concentration of the complex is 4.5×10^{-5} *M* and a 1 cm path-length cell was used. Note that the O.D. scale for the IL band is different from the M→LCT band.

b. Photochemistry

Both the photosubstitution and IL photoisomerization reactivity of *cis*-W(CO)$_4$(*t*-4)$_2$ have been investigated. Additionally, biacetyl sensitized reaction was attempted. Irradiation of the complex in either degassed CH$_2$Cl$_2$ or benzene solution does lead to the *trans*→*cis* conversion of 4-styrylpyridine. The process is very inefficient at 436 nm, but upon irradiation with light of shorter wavelengths, and particularly 313 nm, the quantum efficiency for the process is respectable. Initial isomerization quantum yields are given in Table 2 along with values for other complexes.

The lack of reactivity at 436 nm is unprecedented, and we thus carried out experiments to determine whether (i) competing photochemistry (substitution) precludes IL isomerization or (ii) a state capable of isomerization is achieved but largely relaxes to the *trans* isomer. We find that photosubstitution upon irradiation at 436 nm does not occur efficiently, having a quantum efficiency $\leqslant 0.001$ under conditions where *cis*-W(CO)$_4$py$_2$ substitutes with a quantum efficiency of

TABLE 2

PHOTOISOMERIZATION OF COORDINATED *trans*-4-STYRYLPYRIDINE (*t*-4)

Complex	Φ			
	436 nm	366 nm	313 nm	254 nm
cis-W(CO)$_4$(*t*-4)$_2$ [a]	0.001 (CT,LF)	0.02 (IL,LF,CT)	0.1 (IL)	0.05 (IL,CT)
fac-ClRe(CO)$_3$(*t*-4)$_2$ [b]	—	0.54 (IL)	0.49 (IL)	—
fac-BrRe(CO)$_3$(*t*-4)$_2$ [b]	—	0.51 (IL)	0.64 (IL)	—
W(CO)$_5$(*t*-4) [c]	0.49 (LF,CT)	0.34 (LF,CT)	0.26 (IL)	0.21 (IL,CT)
Ru(bipy)$_2$(*t*-4)$_2$$^{2+}$ [d]	0.05 (CT)	0.05 (LF,CT)	0.15 (IL)	—
ClRu(bipy)$_2$(*t*-4)$^+$ [d]	0.03$_5$ (CT)	—	0.09$_2$ (IL)	—
Free *t*-4 [b]	—	—	0.37—0.39	0.39 [e]

[a] This work; 5—10°C in CH$_2$Cl$_2$; the nature of the excited state achieved directly is indicated in parentheses. [b] Ref. 18. [c] Ref. 9. [d] Ref. 11a. [e] Ref. 25.

~0.3 [12]. Thus, the *cis*-$W(CO)_4(t\text{-}4)_2$ is effectively photosubstitution inert by usual standards for this class of compounds. The lack of reactivity with respect to substitution is likely a consequence of the fact that the lowest excited state is M→LCT in character. Such states are proving to be generally substitution inert [12,14,17—19]. The significance of this result in the present context is that substitution inertness is valuable in that this allows IL reactions to be studied in detail without decomposition of the complex.

To test the possibility that the excited state achieved is capable of isomerization but relaxes to largely the *trans*-isomer, we attempted to prepare and study the photochemistry of pure samples of *cis*-tetracarbonylbis(*cis*-4-styrylpyridine)-tungsten (*cis*-$W(CO)_4(c\text{-}4)_2$). However, we were frustrated in isolating this complex as a pure solid. Nonetheless, it could be effectively produced in solution by substitution according to reaction 1. This complex has an electronic spectrum

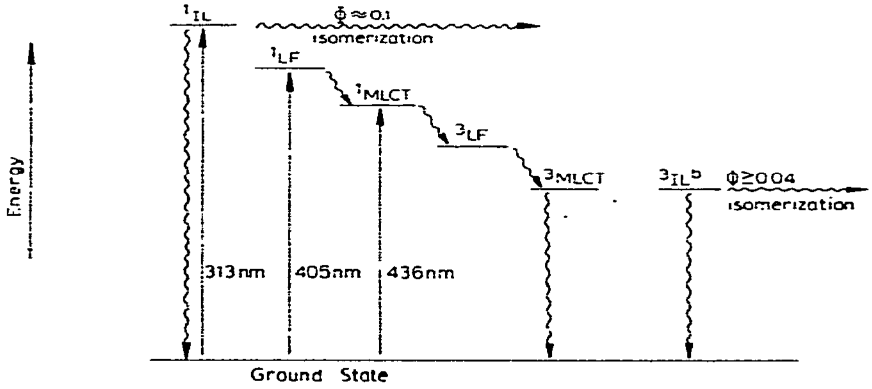
$$cis\text{-}W(CO)_4(\text{piperidine})_2 + \underset{\text{(2-fold excess)}}{cis\text{-4-styrylpyridine}} \xrightarrow[25^\circ C]{\Delta} cis\text{-}W(CO)_4(c\text{-}4)_2 \qquad (1)$$

which is similar to that for the bis(*trans*-4-styrylpyridine) complex, but the bands, except for the band at 400 nm, are blue shifted. But owing to the difficulty in obtaining the pure complex we cannot provide accurate spectral information. Irradiation of the bis(*cis*-4-styrylpyridine) complex at 436 nm under conditions where all of the light is absorbed by the complex does not yield efficient *cis*→*trans* IL isomerization. The quantum yield is found to be ~0.001.

Assuming that the lowest excited state is predominantly W→*c*-4 CT we can tend to rule out the notion that such a state leads to efficient isomerization in this system. The notion that the one-electron transition (M→LCT) reduces the ligand to a radical anion which can isomerize was suggested for the styrylpyridineruthenium(II) complexes [11]. This concept may apply in the system studied here, but the relaxation of the CT state without chemical change (substitution or isomerization) is the dominant primary excited state decay process. Therefore, our complex does not provide a valid test of the notion that the ligand behaves as a coordinated radical anion in the M→LCT excited state.

Since the IL $\pi\rightarrow\pi^*$ spin-allowed transition is easily observable and relatively unperturbed compared to the free ligand, we reasoned that the corresponding spin-forbidden excited state should be equally unperturbed. We investigated the possibility of using triplet sensitization techniques to produce the IL triplet state. The free ligand triplet state so produced undergoes efficient *trans*→*cis* isomerization. Biacetyl, triplet energy ~55 kcal/mole [20], exhibits phosphorescence in well deoxygenated fluid solution at room temperature. For this reason we used excited biacetyl as a donor to investigate the quenching properties of *cis*-$W(CO)_4$-$(t\text{-}4)_2$. We find that this complex quenches the biacetyl triplet at an essentially diffusion controlled rate of $\sim 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. However, this quenching of the biacetyl triplet is not accompanied by highly efficient chemical change in the metal complex. Quantum yields for the biacetyl sensitized *trans* to *cis* isomerization of the coordinated ligand were 0.04 ± 0.02. Unfortunately, large error limits must be assigned here for two reasons: (i) the complex absorbs significantly in the region where biacetyl absorbs and (ii) the complex was found to be somewhat unstable in the presence of biacetyl; presumably thermal redox reactions could occur. However, the significant fact is that the triplet sensitized yield is higher than the low energy direct irradiation isomerization quantum yield. This result indicates that it may be possible to indirectly produce relatively unperturbed IL spin-forbidden excited states. The interesting point in the present system is that the CT triplet state is very likely in an energy range comparable to that for the IL triplet state. Apparently, the donor is capable of, at least partially, producing an IL state capable of isomerization. It would be interesting to study this effect as a function of the triplet energy of the donor. Unfortunately, the present system is not amenable to detailed study because of its intense absorption in the range of interest. Nonetheless, the result that we do have with biacetyl is consistent with the unperturbed nature of the IL states, since free *trans*-4-styrylpyridine quenches biacetyl triplets at a diffusion controlled rate and leads to effective *trans*→*cis* isomerization.

SCHEME 1. Excited state processes in *cis*-$W(CO)_4(t\text{-}4)_2$ ^{a}.



a ——→, radiative process

〰→, non radiative process

b Populated by triplet sensitization

The data support Scheme 1 for the excited state processes. Isomerization obtains from either the direct population of the IL singlet state or the sensitized generation of the IL triplet state. We propose that the triplet M→LCT state is below the lowest LF triplet because the *cis*-$W(CO)_4(t\text{-}4)_2$ is photosubstitution inert. Moreover, the principle pathway for relaxation of the LF and MLCT excited states is very likely through the MLCT triplet. This conclusion follows from the essential wavelength independence (below IL excitations) of the emission quantum yield in related complexes [12,14,18] such as $W(CO)_5$(4-benzoylpyridine) and $W(CO)_4$(1,10-phenanthroline) which are known to emit from M→LCT excited states of triplet character. The relative positions of the IL and MLCT triplets is not clear. However, since the triplet energy of biacetyl is 55 kcal/mole and we do see sensitized isomerization and diffusion controlled quenching, we can conclude that both triplets are accessible with 55 kcal/mole excitation. The interesting result is that the low energy direct irradiation at 436 nm does not result in the state responsible for the sensitized isomerization.

A surprising result is the difference in 436 nm photoreactivity of $W(CO)_5(t\text{-}4)$

[9] and the *cis*-W(CO)$_4$(*t*-4)$_2$. In the pentacarbonyl the lowest state in absorption has considerable LF character whereas in the tetracarbonyl we find mainly CT character on the basis of photosubstitution results. This may mean that the lowest LF triplet can convert to the IL triplet to yield isomerization in the pentacarbonyl. But this hypothesis requires additional testing.

In comparing *cis*-W(CO)$_4$(*t*-4)$_2$ with other complexes, Table 2, we see that an important pattern is emerging. The IL state is relatively reactive in each complex. Moreover, for the ruthenium(II) complexes and the complex studied here, which all have lowest M→LCT excited states in absorption, we see relatively lower reactivity upon irradiation at the longest wavelengths. These facts point to non-interconvertible IL and CT excited states. This may be generally useful in metal complex photoassisted reactions.

Experimental

Materials

Biacetyl, *trans*-4-styrylpyridine, W(CO)$_6$, and *cis*-1,2-bis(diphenylphosphino)-ethylene were all obtained commercially. Biacetyl was freshly distilled prior to use, and W(CO)$_6$ and *trans*-4-styrylpyridine were sublimed before use. All solvents for spectroscopic or photochemical experiments are commercially available and were used as received in spectroscopic grade. *cis*-4-Styrylpyridine was prepared by either direct irradiation of the *trans* isomer or by biacetyl-sensitized photoisomerization. The *cis*-compound was purified by column chromatography on alumina using benzene as the eluant [21]. Purity of the oily liquid was established by gas chromatography and was found to contain $\leqslant$5% of the *trans* isomer.

Synthesis of cis-tetracarbonylbis(trans-4-styrylpyridine)tungsten (cis-W(CO)$_4$-(t-4)$_2$)

This compound was prepared by the thermal reaction of *trans*-4-styrylpyridine with *cis*-W(CO)$_4$(piperidine)$_2$. The latter was prepared by near-UV irradiation of an N$_2$-purged isooctane solution of W(CO)$_6$ and piperidine [12,22]; the *cis* isomer is essentially insoluble in isooctane and precipitates from solution as it forms. The yellow solid is collected by filtration and washed with isooctane repeatedly to remove W(CO)$_5$(piperidine), piperidine, and W(CO)$_6$. The compound undergoes piperidine substitution readily, but in CH$_2$Cl$_2$ an infrared spectrum can be obtained which exhibits bands at 2004, 1890, 1870, and 1825 cm^{-1} in the CO stretching region. This four band pattern is like that for other C_{2v} bis-nitrogen donor complexes having the same coordination sphere. To prepare the *cis*-W(CO)$_4$-(*t*-4)$_2$ complex the *cis*-W(CO)$_4$(piperidine)$_2$ is added to an N$_2$-purged benzene solution of *trans*-4-styrylpyridine (2-fold excess) at 25°C. The solution rapidly turns red-orange reflecting the formation of the desired complex. After spectral changes cease, the benzene solution is rotary evaporated to dryness. The resulting solid is then recrystallized from benzene/n-pentane or CH$_2$Cl$_2$/n-pentane under N$_2$ to remove excess *trans*-4-styrylpyridine. The complex exhibits infrared bands at 2003 w, 1884 m, 1863 m, and 1825 m in the carbonyl stretching region reflecting the C_{2v} symmetry. Decomposition of a weighed sample in air saturated solution yields a stoichiometric amount of *trans*-4-styrylpyridine (2 molecules of *trans*-4-styrylpyridine per W atom).

We attempted to prepare pure samples of *cis*-$W(CO)_4(c\text{-}4)_2$ by a similar procedure, but we were unable to isolate a pure, solid complex. Typically, addition of *cis*-$W(CO)_4$(piperidine)$_2$ to a benzene solution of *cis*-4-styrylpyridine (2-fold excess) yielded spectral changes indicative of complete consumption of *cis*-$W(CO)_4$(piperidine)$_2$ and formation of a new complex. Gas chromatographic analysis at this point reveals that the fraction of the *cis*-4-styrylpyridine present is $\geqslant$95%. However, attempted isolation and recrystallization invariably yielded a complex enriched in *trans*-4-styrylpyridine. Thus, the *cis*-$W(CO)_4(c\text{-}4)_2$ was used as generated in solution.

Spectra

Infrared spectra were recorded on a Perkin—Elmer 180, 521, or 337 spectrometer using 0.1 mm or 1.0 mm matched path length NaCl cells. Electronic spectra were recorded using a Cary 17. Low temperature measurements at 77 K were made using an all-quartz Dewar with optical quality flats for windows. An EPA (ether/isopentane/ethanol, 5 : 5 : 2 by volume) solvent was used for the 77 K measurements. Emission spectra were measured using an Aminco Bowman spectrophotometer equipped with a Hamamatsu R136 PMT detector.

Quenching of biacetyl emission by cis-$W(CO)_4(t\text{-}4)_2$

The quenching of biacetyl triplet states by the complex was studied by measuring the relative emission yield of the biacetyl as a function of complex concentration. The quenching obeys Stern—Volmer kinetics [23] and the quenching constant, k_q, was determined from the slope of the linear Stern—Volmer plots (plots of Φ_0/Φ_Q vs. quencher concentration where Φ_0 is the emission intensity in the absence of quencher and Φ_Q is the emission intensity at a given quencher concentration). The slope of the plot is $k_q\tau$ where τ is the emission lifetime of biacetyl in the absence of quencher. The measurements were made for rigorously freeze-pump-thaw degassed samples of the biacetyl and complex in benzene solutions at 25°C. The value τ was determined using a TRW Model 75 Decay Time Fluorometer equipped with a Xenon Corp. Nanopulser excitation source and a Hamamatsu R446UR PMT detector with the output displayed on a Tektronix 453 oscilloscope.

Irradiations and analyses

All irradiations were carried out using Hanovia 450 or 550 W medium pressure Hg lamps filtered to isolate the 313, 366, or 436 nm Hg emissions. Irradiation at 254 nm was carried out using a UV-Products, Inc. low pressure Hg lamp. Light intensities in quantum yield determinations were measured using ferrioxalate actinometry [24]. Intensities for all irradiations were of the order of 10^{-6}—10^{-7} ein/min. All samples for irradiation were 3.0 ml in volume and were either freeze-pump-thaw degassed or were purged with Ar and sealed. Typically, the solvent for irradiation of the complex was CH_2Cl_2 and the photoreaction temperature was 0—10°C achieved using a cell holder equipped with a circulating system for temperature control. Temperature was maintained using a Forma Scientific circulating bath.

Direct irradiation of *cis*-$W(CO)_4(t\text{-}4)_2$ was monitored by gas chromatography and infrared. A Varian 1400 gas chromatograph with a flame ionization detector using a Model A-25 recorder with a Disc integrator was used. The column was a 5% DEGS (6' × 1/8"), 3% SE-30 (6' × 1/8"), or a 1.5% OV-101 (6' × 1/8") operated at ~170°C. Infrared and gas chromatographic analysis were carried out in parallel to insure that during the course of the irradiation there was no decomposition of *cis*-W(CO)$_4$(*t*-4)$_2$ or *cis*-W(CO)$_4$(*c*-4)$_2$ species.

Biacetyl-sensitized isomerization was carried out in a manner analogous to that for the direct irradiation except that biacetyl was introduced in amounts necessary to absorb most of the light at 436 nm. A correction was made for the fraction of light absorbed directly by the complex. The initial *cis*-W(CO)$_4$(*t*-4)$_2$ concentration was sufficient to quench all biacetyl triplets.

The photosubstitution behavior of *cis*-W(CO)$_4$(*t*-4)$_2$ was investigated by comparison to the photoreactivity of *cis*-W(CO)$_4$(pyridine)$_2$ under identical conditions. The complexes were irradiated in degassed benzene solution in the presence of 0.065 *M* *cis*-1,2-bis(diphenylphosphino)ethylene. As expected [12], *cis*-W(CO)$_4$-pyridine)$_2$ upon 436 nm irradiation, quantitatively yields tetracarbonyl(*cis*l,2-bis(diphenylphosphino)ethylene)tungsten with a quantum yield near 0.3 [12]. Under identical conditions, the *cis*-W(CO)$_4$(*t*-4)$_2$ complex undergoes no detectable change, and we conclude that the photosubstitution efficiency is $\leqslant 0.001$.

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