Intraligand Lowest Excited States in Tricarbonylhalobis(styrylpyridine)rhenium(I) Complexes

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Abstract: The complexes $XRe(CO)_3L_2$ (X = Cl, Br; L = *trans*-3-styrylpyridine, *trans*-4-styrylpyridine) have been synthesized and characterized. Electronic absorption spectral studies reveal that the lowest excited state is an intraligand excited state. Irradiation of the styrylpyridine complexes in the lowest absorption band (313 or 366 nm) results in trans → cis isomerization of the coordinated ligand with a quantum efficiency in the range 0.49–0.64 and stationary states which are no less than 84% cis. Triplet sensitization gives stationary states and quantum yields for the coordinated styrylpyridines which are near those found for the free ligands themselves. Little photosubstitution ($\Phi < 0.01$) of the coordinated styrylpyridine occurs. Thermal substitution of the styrylpyridines at 56° provides a pathway for photoassistance activity of the $XRe(Co)_3L_2$ complexes.

Transition metal photoassisted and photocatalyzed reactions[2] of organic substances potentially represent new approaches to chemical synthesis. Photoassisted reactions[3] require[2] continuous irradiation of some transition metal containing chromophore which is present in catalytic quantities. Thus, like photosensitization, photoassistance may be a means of substrate transformation by an indirect excitation.[4] A general mechanism of photoassistance is shown in reactions 1–3 where at least one of these must be photo-

$$\text{metal} + \text{substrate} \overset{h\nu \text{ or } \Delta}{\rightleftharpoons} [\text{metal–substrate}] \quad (1)$$

$$[\text{metal–substrate}] \overset{h\nu \text{ or } \Delta}{\rightleftharpoons} [\text{metal–transformed substrate}] \quad (2)$$

$$[\text{metal–transformed substrate}] \overset{h\nu \text{ or } \Delta}{\rightleftharpoons} \text{metal} + \text{transformed substrate} \quad (3)$$

chemical. Reaction 2 represents the step at which we might expect novel photochemistry to be found as both (1) and (3) are more or less complicated photosubstitution reactions which are already receiving intense scrutiny both experimentally[5] and theoretically.[6]

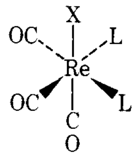
The course of photoinduced reactions of coordinated substrates, reaction 2, is likely to be influenced by (1) the presence of low-lying excited states of the charge transfer (CT) type, (2) perturbation of intraligand (IL) excited states upon coordination, and (3) geometrical structural effects such as having two substrates coordinated to the same metal. Understanding of these factors is relatively primitive as there are few well-studied examples of photoreactions like (2). Some important contributions have been made by study[7] of the d^8 $Fe(CO)_4$–(olefin) complex where photoinduced cis–trans isomerization of the coordinated olefin was found not to involve ligand (olefin or CO) substitution. Wavelength dependent cis–trans photoisomerization phenomena of 4-styrylpyridines coordinated to d^6 Ru(II) have revealed important facts about the interconvertibility of high energy IL and the low-lying Ru(II) → 4-styrylpyridine CT excited states.[8] A comparison[9] of the photochemistry of the d^6 $W(CO)_5(Y)$ (Y = pyridine, *trans*-2-styrylpyridine, *trans*-4-styrylpyridine) complexes showed that efficient cis–trans isomerization of the styrylpyridines could be achieved. This occurs, apparently, at the expense of pyridyl group photosubstitution which likely arises from direct population of a low-lying excited state principally of ligand field (LF) character. We now report the synthesis and characterization of the d^6 complexes $XRe(CO)_3L_2$ (X = Cl, Br; L = *trans*-4-styrylpyridine, *trans*-3-styrylpyridine) which are shown to be unlike either the d^6 Ru(II) or W(0) systems mentioned above. Electronic absorption spectral results, thermal substitution, and photochemical reactions are reported, and these are discussed in terms of photoassistance activity of the $XRe(CO)_3L_2$ species.

Results and Discussion

a. Synthesis and Structure of the Complexes. The $XRe(CO)_3L_2$ complexes are synthesized by the method in the literature[10] for $XRe(CO)_3(py)_2$ (py is pyridine), reaction 4.

$$XRe(CO)_5 \xrightarrow[\text{benzene, L}]{70°} XRe(CO)_3L_2 \quad (4)$$

The details of the synthetic and purification procedure are given in the Experimental Section. The important point to be made is that each of the complexes investigated here has structure I. The ir band maxima in the CO stretching region in Table I evidence the structural similarity of the complexes and confirm[11] the arrangement in I. The pyridyl groups are bonded to the Re through the nitrogen atom.



I

b. Electronic Spectra. The absorption spectra of the $XRe(CO)_3L_2$ complexes and a comparison of these with the spectra of free L, protonated L, and $ClRe(CO)_3(py)_2$ show that the lowest absorption is associated with the IL styrylpyridine transition. The first line of evidence is given in Figure 1 where the 25° absorption spectra of *trans*-4-styrylpyridine, $ClRe(CO)_3(py)_2$, and $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$ (stpy is styrylpyridine) are shown for the same concentration of each species. Note first that the $ClRe(CO)_3(py)_2$ absorptions are relatively weak and the first real maximum falls near 262 nm. The free *trans*-4-styrylpyridine has an absorption maximum at 308 nm (ϵ = 27,900 l. mol^{-1} cm^{-1}) while the $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$ maximum falls to the red at 328 nm (ϵ = 50,300 l. mol^{-1} cm^{-1}) and the band is somewhat broader. The molar extinction coefficients and the band position support the IL assignment. We find additionally that protonation[12] of the free ligand also results in a red-shifted and broadened absorption compared to the nonprotonated form as shown in Figure 2. The first absorption band at 25° of $BrRe(CO)_3(t\text{-}4\text{-stpy})_2$ is nearly identical to that for the chloro analog. Spectra of $ClRe(CO)_3(t\text{-}3\text{-}$

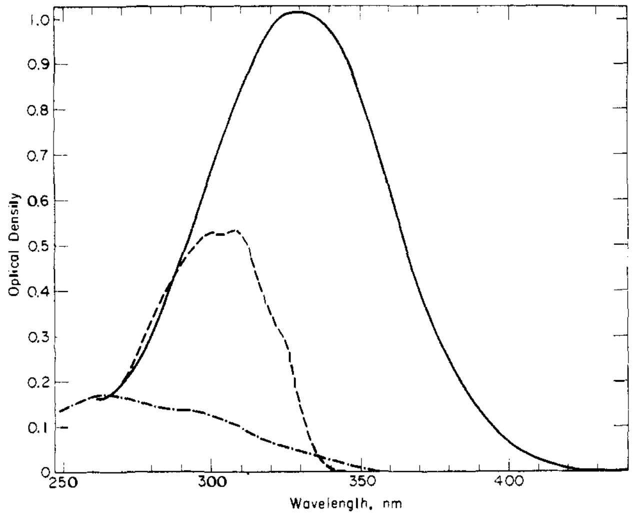


Figure 1. Comparison of absorption spectra of *trans*-4-styrylpyridine (- - -), $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$ (——), and $ClRe(CO)_3(py)_2$ (-·-) all at 1.92×10^{-5} *M* in CH_2Cl_2 solution at 25° in 1.00 cm path length cells.

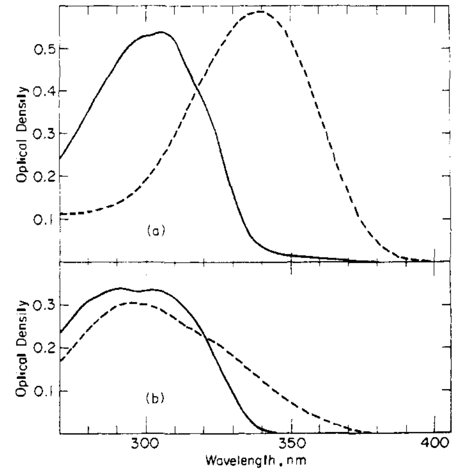


Figure 2. (a) Comparison of absorption of *trans*-4-styrylpyridine at pH 7.0 (nonprotonated, ——) and at pH 2.1 (protonated, - - -) at the same concentration in EtOH: H_2O, 9:1, v/v at 25° in 1.00 cm path length cells. (b) Comparison of absorption of *trans*-3-styrylpyridine at pH 7.0 (nonprotonated, ——) and at pH 2.1 (protonated, - - -) as above.

Table I. Ir Absorption Maxima for $XRe(CO)_3L_2$ in CO Stretching Region[a]

X	L	Bands, cm^{-1}		
Cl	Pyridine	2025	1920	1885
Cl	L_2 = 2,2'-bipyridine	2012	1914	1883
Cl	*trans*-3-Styrylpyridine	2010	1912	1875
Cl	*trans*-4-Styrylpyridine	2020	1920	1882
Cl	*cis*-4-Styrylpyridine	2018	1918	1880
Br	*trans*-4-Styrylpyridine	2017	1916	1883

[a] CH_2Cl_2 solution at 25°.

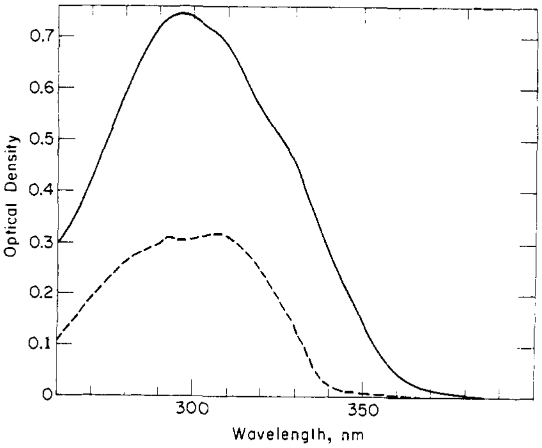


Figure 3. Comparison of absorption spectra of $ClRe(CO)_3(t\text{-}3\text{-stpy})_2$ (——) and *trans*-3-styrylpyridine (- - -) both at 1.66×10^{-5} *M* in CH_2Cl_2 solution at 25° in 1.00 cm path length cells.

stpy)$_2$ and *trans*-3-styrylpyridine at 25° are remarkably similar, Figure 3, but again the complex which contains two chromophores per Re has a molar extinction coefficient nearly twice that of the free ligand: 45,300 vs. 19,300 l. mol^{-1} cm^{-1}. The lack of a pronounced red shift in the absorption like that found for the *trans*-4-styrylpyridine again parallels protonation studies of the free ligand with protonated and nonprotonated *trans*-3-styrylpyridine having quite similar spectra, Figure 2. The room temperature band maxima and extinction coefficients for all of the compounds are summarized in Table II.

Low-temperature spectroscopy substantiates the IL assignment in the styrylpyridine complexes. A comparison of the 298 and 77°K spectra of the complexes and free ligands in EPA appears in Figures 4 and 5. Generally, the 77°K spectra reveal vibrational structure in accordance with the IL assignment. The spectra of both ligands and complexes tend to red shift somewhat upon cooling the samples from 298 to 77°K. For both $ClRe(CO)_3(py)_2$ and $ClRe(CO)_3$(phen) (phen is 1,10-phenanthroline) the lowest absorptions likely have substantial Re → ligand CT character and the absorption band maxima blue shift upon cooling from 298 to 77°K in EPA.[13] Likewise, the M → ligand CT absorption in the d^6 $M(CO)_4$(phen) (M = Cr, Mo, W) complexes blue shifts with decreasing temperature in EPA.[14] The low-temperature spectra of *trans*-3-styrylpyridine and the $ClRe(CO)_3(t\text{-}3\text{-stpy})_2$ each show rich vibrational structure at 77°K but none of the maxima are superimposable putting to rest any possibility of contamination by free L. Finally, the low-temperature spectra of the protonated free ligands, Figure 6, show a remarkable similarity to the low-temperature spectra of $XRe(CO)_3L_2$ species. This is particularly notable for the *trans*-3-styrylpyridine case where a very clear pattern for the vibrational structure is seen. In summary, the absorption spectra of the $XRe(CO)_3(stpy)_2$ complexes show the unique fact that the IL styrylpyridine transition gives rise to the lowest energy absorption in these metal carbonyls.

The $XRe(CO)_3L_2$ complexes exhibit no detectable fluorescence at 25° in solution. This represents a spectroscopic distinction from either the protonated styrylpyridines or the nonprotonated form which all show luminescence. The lack of fluorescence is particularly noteworthy for $ClRe(CO)_3(t\text{-}3\text{-stpy})_2$ since *t*-3-stpy has a substantially higher fluorescence efficiency upon protonation.[12] Thus, while absorption spectra reveal that protonation and coordination to Re break the symmetry of the styrylpyridine in a very similar fashion, the Re has some different influence in the way the excited state decays. Consequently, we have investigated the chemical results of photoexcitation of these molecules and these are developed in the next section.

c. Irradiation of $XRe(CO)_3L_2$. The Re carbonyl-*trans*-styrylpyridine complexes are all photosensitive with respect to trans → cis isomerization of the coordinated olefin. Initial trans → cis isomerization quantum yields for 313- and 366-nm irradiations are set out in Table III along with ultimate trans–cis ratios. Spectral changes in the $XRe(CO)_3L_2$ complexes accompanying the trans → cis isomerizations are depicted in Figures 7 and 8. Fairly good isosbestic points

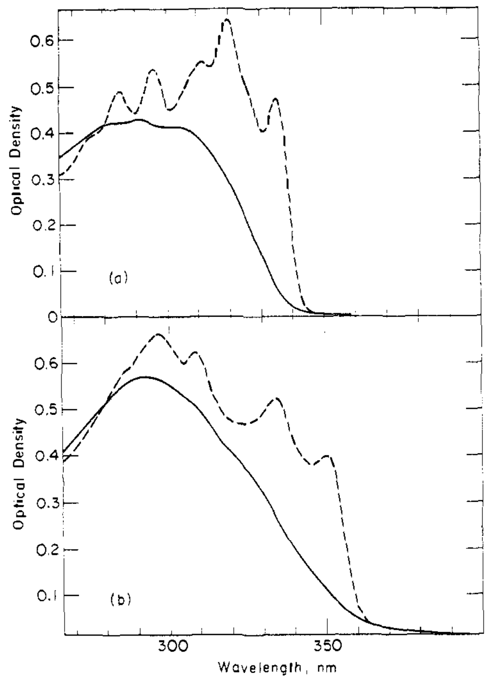


Figure 4. (a) Absorption of *trans*-3-styrylpyridine at 298°K (——) and 77°K (- - -) in EPA. (b) Absorption of $ClRe(CO)_3(t\text{-}3\text{-stpy})_2$ at 298°K (——) and 77°K (- - -) in EPA.

Table II. Ultraviolet Absorption Maxima of Styrylpyridine and Complexes at 25°

Compd	Solvent	Absorption max, nm (ε)
trans-3-Styrylpyridine	CH_2Cl_2	308 (19,300)
	H_2O–EtOH (9:1) pH 7.0	304 (~19,000)
	H_2O–EtOH (9:1) pH 2.1	296 (~19,000)
trans-4-Styrylpyridine	CH_2Cl_2	308 (27,900)
	H_2O–EtOH (9:1) pH 7.0	306 (~28,000)
	H_2O–EtOH (9:1) pH 2.1	338 (~28,000)
$ClRe(CO)_3(t\text{-}3\text{-stpy})_2$	CH_2Cl_2	297 (45,300)
$ClRe(CO)_3(t\text{-}4\text{-stpy})_2$	CH_2Cl_2	328 (50,300)
$BrRe(CO)_3(t\text{-}4\text{-stpy})_2$	CH_2Cl_2	330 (53,200)
$ClRe(CO)_3(py)_2$	CH_2Cl_2	262 (9000)

are observed in Figures 7 and 8, but there is no evidence supporting the notion that isomerization of both coordinated styrylpyridines occurs with one photon. We feel, therefore, that the quantum yields are for reaction 5. A similar

$$XRe(CO)_3(t\text{-stpy})_2 \xrightarrow{h\nu} XRe(CO)_3(t\text{-stpy})(c\text{-stpy}) \quad (5)$$

assumption was made for bis(styrylpyridine)Ru(II) complexes where spectral changes accompanying cis-trans photoisomerization also showed isosbestic points.[8]

In a plot of the percent *trans*-4-styrylpyridine as a function of 436 nm irradiation time of $XRe(CO)_3(t\text{-}4\text{-stpy})_2$ we find no break in the smooth curve which ultimately shows essentially no remaining trans olefin. This information suggests that reaction 6 occurs with a quantum yield not

$$XRe(CO)_3(t\text{-stpy})(c\text{-stpy}) \xrightarrow{h\nu} XRe(CO)_3(c\text{-stpy})_2 \quad (6)$$

substantially different from reaction 5. This fact is consistent with the apparent lack of electronic interaction of the two styrylpyridines inferred from the absorption spectra.

The product of reaction 6 can be isolated and purified by recrystallization with no cis–trans isomerization of the coordinated styrylpyridines. For the 4-styrylpyridine complexes which do absorb at 436 nm the complete conversion to the product in reaction 6 can be achieved by 436-nm photolysis, and, importantly, no decomposition of the complex could be detected. Indeed, we note the essential lack of ($\Phi < 0.01$) photosubstitution involving the styrylpyridines at 25°. One final note about the direct photolysis of $XRe(CO)_3L_2$ complexes concerns the possibility of CO dissociation. Prolonged photolysis, even at 436 nm, in the presence of added L produces orange-colored products. These products have not been identified, but may involve CO substitution. In any case, the reaction quantum yield for this process is very small ($<10^{-3}$) and represents only a very small fraction of the excited state decay.

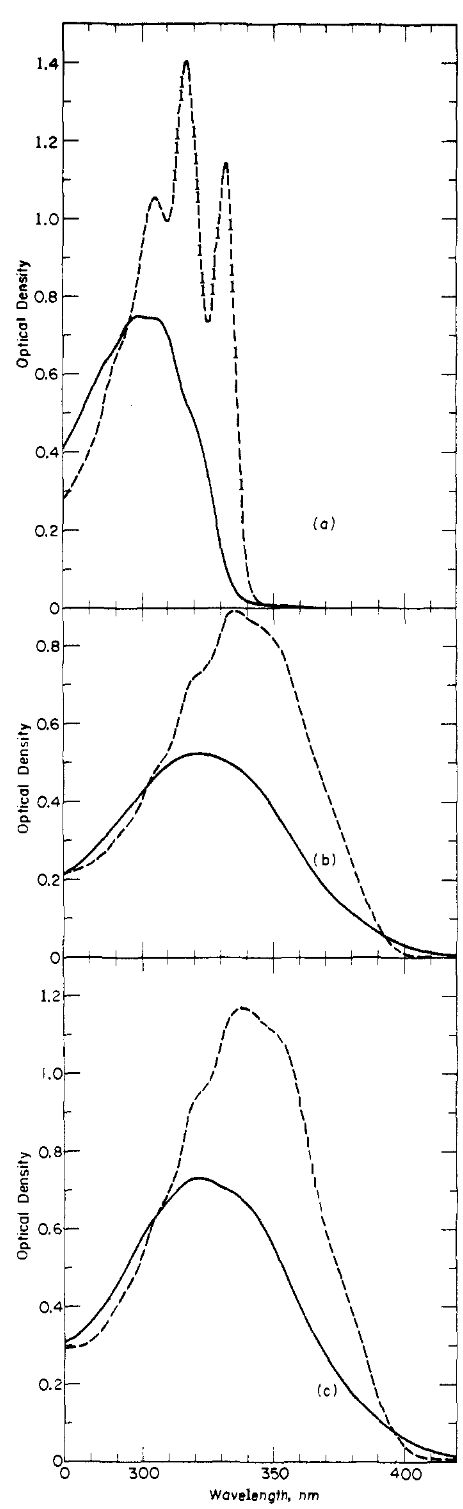


Figure 5. Spectra at 298°K (——) and 77°K (- - -) in EPA for (a) *trans*-4-styrylpyridine, (b) $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$, and (c) $BrRe(CO)_3(t\text{-}4\text{-stpy})$.

Table III. Direct Photolysis Isomerization of Coordinated Styrylpyridines[a]

Compd	Φ (t → c) 313 nm	Φ (t → c) 366 nm	% cis at PSS ± 2 313 nm	366 nm	436 nm
trans-3-Styrylpyridine	0.48[b]	*c*	90[d]	*c*	*c*
trans-4-Styrylpyridine	0.38[e]	*c*	88[f]	*c*	*c*
$ClRe(CO)_3(t\text{-}4\text{-}stpy)_2$	0.49	0.54	84	90	99
$BrRe(CO)_3(t\text{-}4\text{-}stpy)_2$	0.64	0.51	99	98	>99
$ClRe(CO)_3(t\text{-}3\text{-}stpy)_2$	0.60	0.51	93	90	99

[a] CH_2Cl_2 solutions at 25°; light intensity ~10^{-7} Einstein/min; Φ's are ±10%. [b] Literature values are 0.43, ref 15, and 0.52, ref 12. [c] No absorption at these wavelengths. [d] Reference 12. [e] Literature values are 0.37, ref 15, and 0.39, ref 12. [f] Reference 15.

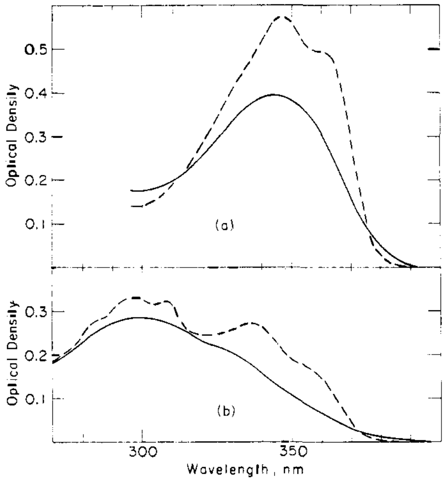


Figure 6. Spectra at 298°K (——) and 77°K (- - -) in EtOH at pH 2 for (a) *trans*-4-styrylpyridine and (b) *trans*-3-styrylpyridine. At this pH each species is fully protonated.

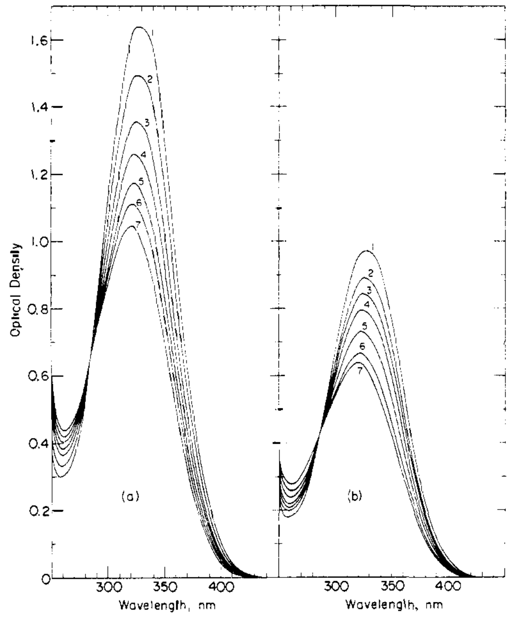


Figure 7. Uv-visible spectral changes accompanying 366 nm photolysis of (a) $BrRe(CO)_3(t\text{-}4\text{-}stpy)_2$ and (b) $ClRe(CO)_3(t\text{-}4\text{-}stpy)_2$ at 25° in CH_2Cl_2. Curve 1 corresponds to 100% *trans*-4- and curve 7 to ~95% *cis*-4-styrylpyridine coordinated to the Re.

The triplet-sensitized reaction of the styrylpyridines has been investigated.[15,16] We have investigated some aspects of the triplet-sensitized reaction of $ClRe(CO)_3(t\text{-}stpy)_2$ to complete the characterization of the photoisomerization reactivity of the complexed olefin. Some relative quantum yield and stationary state information is summarized in Table IV. As with the free olefin, benzil (triplet energy, $E_T \approx 54$ kcal/mol)[17] sensitized isomerization of the coordinated olefin yields a stationary state cis–trans ratio which is extremely cis rich. Michler's ketone ($E_T \approx 61$ kcal/mol)[17] gives a stationary state for both the free and the coordinated olefin which reflects its ability to transfer triplet excitation to *cis*-styrylpyridine ($E_T \approx 57$ kcal/mol).[18] The extremely high percentage cis at the benzil triplet stationary state is presumably due to the slow, endothermic energy transfer from benzil to the cis olefin. $Ru(bipy)_3{}^{2+}$ ($E_T \approx 48$ kcal/mol)[16] likewise produces highly cis rich stationary states. The benzil triplet sensitized quantum yield for the trans → cis isomerization of the coordinated ligand is very close to the free ligand value.

The photochemistry of the $XRe(CO)_3L_2$ is consistent with the fact that the IL state is lowest in energy. The excited state decay is dominated by trans → cis isomerization of the coordinated ligand and this occurs with efficiencies which are very similar to those for the free ligands. Even the triplet-sensitization studies show little difference between the free ligands and the $XRe(CO)_3L_2$ complexes. Thus, the only definitive change in excited state decay behavior remains the lack of detectable fluorescence from the styrylpyridine complexes. We could tentatively associate this lack of fluorescence with an enhanced rate of intersystem crossing due to the presence of the third row Re atom. The fact that the sensitized and direct quantum yields for reaction are the same is consistent with, but by no means proves, the possibility that the triplet state is responsible for the trans → cis isomerization of the coordinated ligand. In this regard we note the lack of any evidence for a direct singlet → triplet IL absorption band in the $XRe(CO)_3L_2$ complexes. Such an absorption should accompany a heavy atom perturbation. An unequivocal measure of the role of Re as a heavy atom will await the results for other cases where the IL state is lowest.

d. $XRe(CO)_3L_2$ Photoassisted Isomerization. Since the optical absorption spectrum of free L and coordinated L are different, especially for L = *trans*-4-styrylpyridine where the absorption of coordinated L is substantially red shifted, there is some reason to investigate the photoassistance activity of the $XRe(CO)_3L_2$ species. To illustrate, the complete conversion of *trans*-4-styrylpyridine to *cis*-4-styrylpyridine could be achieved by 436-nm photolysis of a catalytic amount of $ClRe(CO)_3(t\text{-}4\text{-}stpy)_2$ if the products indicated in (5) or (6) or both are substitution labile with respect to 4-styrylpyridine exchange. We have already pointed out that photosubstitution of the L in $XRe(CO)_3L_2$ is very inefficient, and, further, thermal substitution of L at 25° is extremely slow. Thus, photoassistance activity at 25° according to a scheme as in eq 1–3 is thwarted by slow regeneration of a Re carbonyl species having a *trans*-4-styrylpyridine IL absorption. After finding that substitution reactivity of L in $XRe(CO)_3L_2$ increases markedly upon increasing the temperature to 56°, we have investigated some factors influencing the rate of thermal substitution and the photoassistance activity of $ClRe(CO)_3(t\text{-}4\text{-}stpy)_2$ at 56 and 25°.

Heating solutions of $XRe(CO)_3L_2$ in the presence of

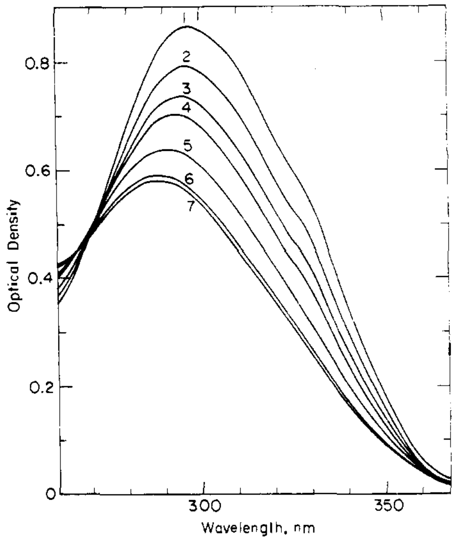


Figure 8. Uv-spectral changes accompanying 366-nm photolysis of $ClRe(CO)_3(t\text{-}3\text{-stpy})_2$ at 25° in CH_2Cl_2 solution. Curve 1 corresponds to 100% *trans*-3- and curve 7 to ~90% *cis*-3-styrylpyridine coordinated to the Re.

1,10-phenanthroline leads completely and irreversibly to $XRe(CO)_3(phen)$. Some initial rate data for the reaction at 56° in CH_2Cl_2 are summarized in Table V. The data reveal that: (1) the observed initial rate is independent of 1,10-phenanthroline concentration when no other entering groups are present; (2) the initial rate of product formation is suppressed by added L; (3) the observed rate of product formation is proportional to $XRe(CO)_3L_2$ concentration. All of this is consistent with a mechanism like that given in reactions 7-9 where the dissociation of L (reaction 7) is the

$$XRe(CO_3)L_2 \xrightarrow{k_{\text{dissoc}}} XRe(CO)_3L + L \tag{7}$$

$$XRe(CO)_3L + L \longrightarrow XRe(CO)_3L_2 \tag{8}$$

$$XRe(CO)_3L + 1,10\text{-phenanthroline} \longrightarrow XRe(CO)_3(phen) + L \tag{9}$$

rate-limiting step. The capture of 1,10-phenanthroline and the concomitant extrusion of L in $XRe(CO)_3L$ has precedence in that $W(CO)_4(py)$ photogenerated from $c\text{-}W(CO)_4(py)_2$ similarly yields directly $W(CO)_4(phen)$.[14] The data for the rate of formation yield, then, a minimum value for k_{dissoc} which is obtained by dividing the observed initial rate by the initial $XRe(CO)_3L_2$ concentration. The values of k_{dissoc} are 0.72, 0.87, and 2.55 × 10^{-4} sec^{-1} for L = *trans*-4-styrylpyridine, *cis*-4-styrylpyridine, and *trans*-3-styrylpyridine, respectively. These rates are large enough to allow styrylpyridine exchange to occur sufficiently fast to expect photoassistance to occur by the mechanism in Scheme I. Two points are noted here. First, electronic excitation remains the pathway for isomerization and the reaction is not catalytic with respect to photons but is catalytic with respect to Re. Second, the effective quantum efficiency for photoassisted isomerization of excess *trans*-styrylpyridine will depend on the light intensity over a certain range. If the light intensity is large enough, the $ClRe(CO)_3(c\text{-stpy})_2$ species will be the principal light-absorbing species since the photostationary state amounts of $ClRe(CO)_3(t\text{-stpy})_2$, $ClRe(CO)_3(c\text{-stpy})(t\text{-stpy})$, and $ClRe(CO)_3(c\text{-stpy})_2$ will depend on both the thermal styrylpyridine exchange rate and the trans-cis photoisomerization rate. When thermal ligand exchange and trans-cis photoisomerization are competitive in a temporal sense then the quantum yield for isomerization of the excess ligand will be intermediate between zero and the initial quantum yield for the trans → cis isomerization in $ClRe(CO)_3(t\text{-stpy})_2$. Only when thermal exchange far exceeds the rate at which photons are absorbed will the isomerization quantum yield for excess *trans*-styrylpyridine approach the upper limiting value for the quantum yield of the coordinated ligand.

Scheme I

$$ClRe(CO)_3(t\text{-stpy})_2 \xrightarrow{h\nu} ClRe(CO)_3(c\text{-stpy})(t\text{-stpy})$$

$$ClRe(CO)_3(t\text{-stpy})(c\text{-stpy}) \xrightarrow{h\nu} ClRe(CO)_3(c\text{-stpy})_2$$

$$ClRe(CO)_3(t\text{-stpy})(c\text{-stpy}) + \textit{trans} \overset{\Delta}{\rightleftharpoons} ClRe(CO)_3(t\text{-stpy})_2 + c\text{-stpy}$$

$$ClRe(CO)_3(c\text{-stpy})_2 + t\text{-stpy} \overset{\Delta}{\rightleftharpoons} ClRe(CO)_3(t\text{-stpy})(c\text{-stpy})$$

Table IV. Triplet-Sensitized Isomerization of Coordinated Styrylpyridines

Compd	Sensitizer	$\Phi_{t\rightarrow c}$	% cis at PSS
trans-4-Styrylpyridine	Benzil	0.40[a]	99
	Michler's ketone		67
	$Ru(bipy)_3^{2+}$	0.4 ± 0.05[b]	96.5 ± 1.0[b]
$ClRe(CO)_3(t\text{-4-stpy})_2$	Benzil	0.5	99
	Michler's ketone		70
	$Ru(bipy)_3^{2+}$		96
trans-3-Styrylpyridine	Benzil	0.44[a]	99
$ClRe(CO)_3(t\text{-3-stpy})_2$	Benzil	0.5	99
	$Ru(bipy)_3^{2+}$	~0.4	93

[a] Assumed to be equal to benzophenone value, ref 15. [b] Reference 16.

Table VI summarizes the data for a typical $ClRe(CO)_3(t\text{-4-stpy})_2$ photoassisted isomerization of *trans*-4-styrylpyridine. At 25°, where styrylpyridine exchange is slow, the amount of *cis*-styrylpyridine present as a function of 436 nm irradiation time rapidly approaches the limiting amount predicted on the basis of the stationary state (Table III) of $ClRe(CO)_3(t\text{-4-stpy})_2$ present. However, at 56° the amount of isomerization that occurs exceeds the amount of styrylpyridine initially coordinated to Re and the observed quantum yield for isomerization only drops off to about 40% of the initial yield. At 25° the photoassistance activity is indeed very small as expected if no ligand exchange occurs. Even at 56°, the slow thermal exchange rate apparently retards the isomerization quantum efficiency at the ~1 × 10^{-6} Einstein/min light level.

Summary

Absorption spectral studies of $XRe(CO)_3L_2$ (X = halogen; L = styrylpyridine) show that the lowest excited states of these complexes are intraligand states associated with the styrylpyridine chromophore. Though the absorptions are red shifted compared to the free ligand the trans → cis photoisomerization reactivity of the complexed and the free styrylpyridine are very similar. The red-shifted absorptions have been exploited to achieve the $ClRe(CO)_3L_2$ photoassisted isomerization of added styrylpyridine by irradiation in the low-energy region of the first absorption band of $ClRe(CO)_3L_2$ where the free styrylpyridine does not absorb. The demonstration that the excited state reactivity of the styrylpyridine is not vastly perturbed upon coordination prompts further chemical exploration of systems of this kind to take advantage of the geometrical proximity of the coordinated ligands.

Experimental Section

Materials. The *trans*-4-styrylpyridine was obtained from Eastman Chemical Co. and the *trans*-3-styrylpyridine was supplied by

Table V. Thermal Conversion of $ClRe(CO)_3L_2$ to $ClRe(CO)_3(phen)$ at 56°[a]

L	$ClRe(CO)_3L_2$, *M*	Phen, *M*	Added L, *M*	Obsd initial[b] rate, mol l.$^{-1}$ sec^{-1}
trans-4-Styrylpyridine	1.77×10^{-4}	6.62×10^{-3}	None	1.31×10^{-8}
	1.77×10^{-4}	1.89×10^{-2}	None	1.38×10^{-8}
	1.77×10^{-4}	3.66×10^{-2}	None	1.29×10^{-8}
	1.77×10^{-4}	2.43×10^{-1}	None	1.15×10^{-8}
cis-4-Styrylpyridine	1.77×10^{-4}	5.48×10^{-2}	None	1.54×10^{-8}
	1.77×10^{-4}	1.79×10^{-1}	None	1.54×10^{-8}
trans-4-Styrylpyridine	2.49×10^{-4}	4.77×10^{-2}	None	1.70×10^{-8}
	6.48×10^{-4}	4.77×10^{-2}	None	4.33×10^{-8}
	2.19×10^{-3}	4.77×10^{-2}	None	1.62×10^{-7}
trans-4-Styrylpyridine	6.59×10^{-4}	4.02×10^{-2}	None	4.79×10^{-8}
	6.59×10^{-4}	4.02×10^{-2}	4.78×10^{-2}	2.66×10^{-8}
	6.59×10^{-4}	4.02×10^{-2}	1.31×10^{-1}	9.22×10^{-9}
trans-3-Styrylpyridine	2.49×10^{-4}	4.77×10^{-2}	None	7.70×10^{-8}
	6.48×10^{-4}	4.77×10^{-2}	None	1.52×10^{-7}
	1.54×10^{-3}	4.77×10^{-2}	None	3.42×10^{-7}

[a] Carried out in 3.0 ml CH_2Cl_2 solutions in 1.00 cm path length stoppered cuvettes. [b] Initial rate of $ClRe(CO)_3(phen)$ formation by measuring increase in optical density at 450 nm, $\epsilon = 940$ l. mol^{-1} m^{-1}.

Table VI. $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$ Photoassisted Isomerization of *trans*-4-Styrylpyridine[a]

Photolysis[b] time, min	% conversion[c] 25°	56°
10	0.91	0.78
25	1.85	2.00
45	3.00	3.75
80	4.07	5.40
147	4.69	7.73
213	5.34	9.47
270	5.44	11.11

[a] Initially 0.11 *M* *trans*-4-styrylpyridine, 0.0035 *M* $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$ in CH_2Cl_2. At the outset 5.98% of all styrylpyridine present is coordinated to Re. [b] Photolysis of 2.00 ml samples of above solution at 436 nm in a stoppered cuvette. Light intensity is approximately 1×10^{-6} Einstein/min. The sample cuvette was placed in a cell holder and thermostated at the indicated temperature. [c] Percent *cis*-4-styrylpyridine at indicated photolysis time.

Professor D. G. Whitten of the University of North Carolina. Both $ClRe(CO)_5$ and $BrRe(CO)_5$ were purchased from Pressure Chemical Co. The $ClRe(CO)_3(py)_2$ and $ClRe(CO)_3(2,2'\text{-bipy})$ were those synthesized and characterized previously.[13] All solvents used were free of absorbing impurities in the regions of interest and are commercially available.

The $XRe(CO)_3L_2$ complexes were prepared as outlined in the literature.[10,11,13] The synthesis and characterization of one complex, $BrRe(CO)_3(t\text{-}4\text{-stpy})_2$, will be described here. The $BrRe(CO)_5$ (~0.2 g) and *trans*-4-styrylpyridine (~0.2 g) were dissolved in 250 ml of benzene. The initially colorless solution was heated to 70° for 5 hr. During the entire period the solution was stirred and kept in the dark. The yellow solution was rotary evaporated to dryness to yield the off-white product and the residual starting materials. The solid was dissolved in a minimum amount of CH_2Cl_2 and addition of *n*-pentane precipitated the product. Filtration followed by a second crystallization removed (by ir and uv spectra) the starting materials and yielded an analytically pure complex. A C, H, N analysis was done by Alfred Bernhardt. Anal. Calcd for $BrRe(CO)_3(t\text{-}4\text{-stpy})_2$: C, 48.84; H, 3.08; N, 3.93. Found: C, 48.19; H, 3.21; N, 3.89. Ir bands in CH_2Cl_2 are at 2020 (s), 1920 (mn), and 1880 (mn) cm^{-1} and the uv maximum is at 328 nm, ϵ = 53,200 l. mol^{-1} cm^{-1}. The coordinated olefins are ~100% trans as determined gas chromatographically.

Spectra. Ir spectra were obtained using either a Perkin-Elmer 337 or 521 instrument with matched path length 0.1 or 1.0 mm NaCl cells. All uv-visible absorption measurements were obtained with a Cary 17 uv-visible-nir spectrophotometer. Luminescence measurements were made using an Aminco Bowman spectrophotofluorometer. Measurements at 77°K were performed using an all quartz liquid N_2 Dewar with optical quality flats for windows. For the 77°K measurements EPA was generally used as a solvent. Comparison spectra of the styrylpyridines at pH 7.0 (nonprotonated) and pH 2.1 (protonated) were measured using H_2O:EtOH 9:1 v/v as the solvent. The pH was measured using a Corning pH meter with a combination electrode. The pH 2.1 was achieved by addition of a small amount of concentrated HCl to the solution. Two drops of a pH 7.0 buffer was added to the solvent to achieve pH 7.0 for the spectral measurement. Low-temperature (77°K) spectra of the protonated styrylpyridine were taken using EtOH as the solvent with a small amount of added HCl(aq). The changes in spectra which occur upon cooling from 298 to 77°K shown in the figures have not been corrected for solvent contraction.

Styrylpyridine Photoisomerization. The isomeric styrylpyridines either as the free ligand or coordinated were analyzed by gas chromatography. A 5 ft × ⅛ in., 5% DEGS on 60–80 Chromosorb G column was used at 180° (injector at 220°) in a Varian 2400 gas chromatograph equipped with a flame ionization detector. The complexes were analyzed just by injection of 1.0-μl samples of the $XRe(CO)_3L_2$ in CH_2Cl_2 or benzene solution. The retention times for L and L from the thermal decomposition of the complex are very nearly the same though there is slightly more tailing for the complex. Also, comparison with an internal standard reveals that free L and complexed L give the same peak area at equal concentrations. Benzil trans → cis sensitizations were measured by comparison of the cis area to the benzil area since benzil elutes prior to, or on top of, the *trans*-styrylpyridine. The relative response of *cis*-styrylpyridine and benzil was determined by injection of known mixtures of *cis*-styrylpyridine and benzil.

Irradiations. Irradiations were carried out using 450 or 550 W medium pressure Hanovia Hg lamps filtered with appropriate Corning glass and solution filters to isolate the 313, 366, 405, 436, or 550 nm Hg emission. The solutions to be irradiated were placed in 13 × 100 mm Pyrex test tubes and irradiated in a merry-go-round.[19] The light intensities were determined by ferrioxalate actinometry[20] and were of the order of 10^{-7} Einstein/min. Except for $Ru(bipy)_3^{2+}$ sensitization, all photochemistry was carried out in CH_2Cl_2, benzene, or CH_2Cl_2/benzene 4:1 v/v. For the $Ru(bipy)_3^{2+}$ case some EtOH was required to dissolve the $Ru(bipy)_3Cl_2$ salt. For direct irradiations the sample, either L or $XRe(CO)_3L_2$, was weighed directly into the test tube and 3 ml of the solvent was added by pipet. Typically, the concentration of $XRe(CO)_3L_2$ used was 0.005 *M*. For sensitized irradiation the samples were freeze-pump-thaw degassed in at least three cycles using 13 × 100 Pyrex test tubes with constrictions for hermetic sealing. For benzil sensitization the quantum yields for *trans* → *cis*-4-styrylpyridine isomerization were carried out at a concentration of the $XRe(CO)_3L_2$ which quenched 100% of the benzil triplets, as evidenced by quenching of the benzil phosphorescence. The benzil sensitization was carried out at 436 nm. Michler's ketone sensitization was carried out at 405 nm such that it absorbed >90% of the incident light, and $Ru(bipy)_3^{2+}$ sensitization was carried out at either 436 or 550 nm. Quantum yields are for small conversion, <10%, in both direct and sensitized cases.

Substitution of L in $XRe(CO)_3L_2$. The probe for substitution activity of L in $XRe(CO)_3L_2$ was substitution of the ligands L by 1,10-phenanthroline. Heating benzene solutions of $XRe(CO)_3L_2$

and 1,10-phenanthroline to 56° yields rapid and nearly quantitative formations of $XRe(CO)_3(phen)$ as identified by ir and uv-visible spectra compared to authentic samples of the product. The $XRe(CO)_3(phen)$ is sparingly soluble in benzene and crystallizes from solution upon cooling from 56 to 25°. The typical procedure for quantitative measure of the substitution rate is given by the following: 0.0007 g of $ClRe(CO)_3(t\text{-4-stpy})_2$ and 0.0564 g of 1,10-phenanthroline were dissolved in 3.0 ml CH_2Cl_2. The solution was placed in a stoppered 1.00-cm path length cuvette and placed in the Cary 17 cell holder and thermostated to 56°. The optical density increase at 450 nm was followed as a function of thermolysis time. An isosbestic point is found at ~398 nm and about 15% conversion to $ClRe(CO)_3(phen)$ obtains in about 2 hr. The molar extinction coefficient for the product at 450 nm at 60° in CH_2Cl_2 is 940 l. mol^{-1} cm^{-1} determined from an authentic sample.

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Unsaturated Organometallic Compounds of the Main Group Elements. The Isolation and Structural Properties of Bis[(tetramethylethylenediamine)lithium(I)] Anthracenide

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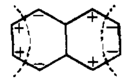
Abstract: Bis[(tetramethylethylenediamine)lithium(I)] anthracenide, $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{14}H_{10}$, has been synthesized from 9,10-dihydroanthracene and *n*-butyllithium tetramethylethylenediamine and the molecular structure determined by single-crystal X-ray structural studies. The anthracenide group in this molecule exhibits structural distortions from the neutral anthracene molecular geometry which are consistent with the symmetry properties of the highest unoccupied molecular orbital of the anthracene molecule. In particular, a significantly nonplanar geometry is observed in keeping with a substantial antiaromatic character in the anthracenide fragment. The greater delocalization possible in anthracene compared to that for naphthalene results in a correspondingly smaller change in the anthracene molecular bond lengths in going from the neutral anthracene to the lithium anthracenide complex. One of the two lithium atoms is located over the central six-membered ring and the other is positioned on the opposite side of the molecule over one of the outer six-membered rings. The configuration for the lithium atom over the outer six-membered ring of the anthracene group is almost identical with that of the lithium atom with respect to the naphthalene fragment in bis[(tetramethylethylenediamine)lithium(I)] naphthalenide. The distances of the lithium atoms from the anthracene ring planes are 2.053 (5) and 1.994 (5) Å. The three-dimensional structure of bis[(tetramethylethylenediamine)lithium(I)] anthracenide was determined from 2462 single-crystal X-ray diffractometer data. The compound crystallizes in the monoclinic space group, $P2_1/c$ with lattice parameters (t = 23°) of a = 8.44 (1) Å, b = 17.43 (2) Å, c = 18.17 (2) Å, β = 91.5 (5)°. The calculated density is 1.06 g cm^{-3} for Z = 4. Least-squares refinement gave a weighted final agreement factor of 0.066.

A recent study[1] of the molecular stereochemistry of bis[(tetramethylethylenediamine)lithium(I)] naphthalenide revealed a number of interesting points. The carbanion geometry was found to be consistent with the symmetry of the highest occupied molecular orbital (HOMO) of the carbanion molecule (below), with an increase in the C(1)–C(2) bond length of 0.07 Å and a corresponding decrease in the C(2)–C(3) bond length of 0.08 Å on the formation of the dianion. The naphthalenide dianion is a 4n π antiaromatic[2]



system and the C(2)–C(3) bond length of 1.343 (8) Å, which is the value expected for a localized double bond as