as a synthetic intermediate in the production of indenyl-lanthanide and -actinide complexes. It has appreciable solubility in aromatic hydrocarbons; $Sm(C_9H_7)_3$,[23] $U(C_9H_7)_3Cl$,[25] and $Sc(C_9H_7)_3$[26] were all initially prepared from toluene solutions of $Mg(C_9H_7)_2$ mixed with the anhydrous metal chloride.

Supplementary Material Available. Calculated hydrogen atom coordinates, best planes results, and the structure factor table will appear, at the request of the Editor, following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-994.

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The Nature of the Lowest Excited State in Tricarbonylchloro-1,10-phenanthrolinerhenium(I) and Related Complexes

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Abstract: Complexes of the general formula $ClRe(CO)_3X$ (X = 1,10-phenanthroline and related ligands) are found to undergo radiative decay from their lowest electronically excited state both in 298°K fluid solution and at 77°K in glassy media. Emission lifetimes are near 10^{-5} sec at 77°K in EPA and at least 1 order of magnitude shorter at 298°K in deoxygenated solutions. Luminescence quantum yields at 77°K are of the order of 10^{-1}. Variations in the lowest absorption maximum with X and solvent polarity are consistent with a M → X π^* charge-transfer (CT) transition. The sensitivity of the emission spectrum to its environment and X point to an association with the M → X π^* CT absorption. Both the emission lifetimes and preliminary energy transfer experiments are consistent with an emitting state which has substantial triplet character. The room temperature fluid solution luminescence observed in these complexes constitutes the first direct observation of excited state decay in metal carbonyls under conditions where photochemistry is normally performed. These complexes also exhibit a unique effect referred to as *luminescence rigidochromism* (spectral distribution of luminescence in fluid media and rigid media is vastly different). In these $ClRe(CO)_3X$ complexes emission maxima shift up to ~1500 cm^{-1} depending on the environmental rigidity, yielding red-orange luminescence in fluid solution and yellow-green luminescence in rigid media.

Excited-state decay processes in metal carbonyl complexes are dominated by ligand dissociation in fluid solution.[1] These processes or internal conversion to electronic states inaccessible by direct absorption must occur very rapidly (~10^{10} sec^{-1}) since no luminescence has been noted for these compounds in solution even though radiative decay rate constants are estimated to be quite large due to high oscillator strengths for observed electronic absorptions.[1,2] To date no one has claimed direct observation, by any technique, of an electronically excited metal carbonyl in fluid solution at room temperature. Indeed, characterization of the electronically excited states of most metal complexes has been by elucidation of excited-state chemistry[3] or by absorption spectrocopy.

The only metal carbonyl complexes known to luminescence at all are low-spin d^6 W, Mo, Cr substituted carbonyl complexes which emit only at low temperatures.[4] The $W(CO)_5L$ luminescence was assigned to the $^3E(e^3b_2{}^2a_1{}^1) \rightarrow {}^1A_1(e^4b_2{}^2)$ ligand field (LF) transition.[4a] Experiments both in rigid media at 77°K and fluid solution at 298°K showed that the ~3 × 10^{-6} sec excited-state lifetime at 77°K shortens to at least 2 × 10^{-11} sec at 298°K in solution for $W(CO)_5$-(py)[5] (py = pyridine). The change in lifetime was attributed to rapid pyridine photodissociation in the 298°K solutions. Some coordination compounds do undergo radiative decay in fluid solution and these include several Cr(III) complexes which give LF luminescence[6] and Ru(II) or Ir(III) tris-1,10-phenanthroline or tris-2,2'-bipyridine complexes which exhibit spin-

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Table I. Absorption Maxima for $ClRe(CO)_3X^a$

X	X^b band max, $cm^{-1} \times 10^{-3}$ ($\epsilon \times 10^{-3}$)	$ClRe(CO)_3X$ Band max, $cm^{-1} \times 10^{-3}$ ($\epsilon \times 10^{-3}$)
1,10-Phenanthroline	38.02 (33.10)	~24.4 sh, 26.53 (4.00), 37.31 (30.62)
5-Methyl-1,10-phenanthroline	37.31 (40.5)	~23.8 sh, 26.32 (4.10), 37.31 (26.75)
4,7-Diphenyl-1,10-phenanthroline	36.76 (36.80)	26.53, 34.97
5-Chloro-1,10-phenanthroline	37.45 (18.08)	~23.8 sh, 25.91 (4.1), 36.76 (30.31)
5-Bromo-1,10-phenanthroline	37.45 (19.50)	~24.0 sh, 25.84 (3.9), 36.50 (27.50)
5-Nitro-1,10-phenanthroline	37.88 (17.10)	~22.0 sh, 25.19 (3.8), 36.63 (27.70)
1,10-Phenanthroline-5,6-dione	38.61 (33.98)	~20.2 sh, 26.32 (3.0), 40.82 (24.30)
2,2'-Biquinoline	30.58 (8.70)^c	~20.8 sh, 22.83 (1.92), 26.67 (20.90)

^{a} CH_2Cl_2, 298°K, sh denotes shoulder. ^{b} Most intense maximum is given except where noted otherwise. ^{c} Most intense maximum of first absorption system; a second more intense absorption is found at 38,460 cm^{-1}.
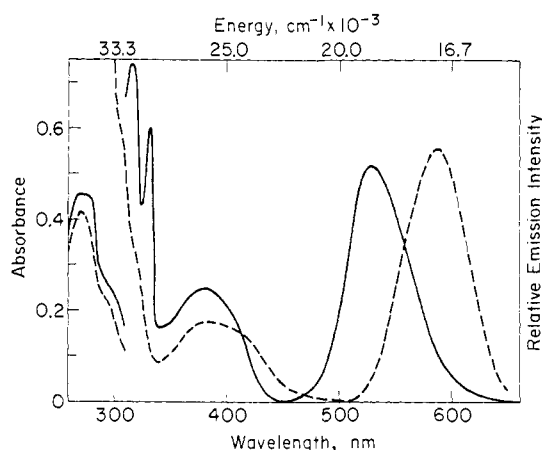

Figure 1. Absorption (left) and emission (right) at 298°K (---) and 77°K (——) of ClRe (CO)₃ (1,10-phen) in EPA. Room temperature absorption maxima are at 26,100 cm^{-1} (ϵ 4000) and 37,030 cm^{-1} (ϵ 30,600). The low temperature spectrum is uncorrected for solvent contraction and the emission at 298 and 77°K were not recorded at the same sensitivity.

Figure 2. Absorption spectrum of 7.8×10^{-5} M $ClRe(CO)_3$-$(py)_2$ at 298°K in CH_2Cl_2 in a 1.0-cm path length cell.

forbidden charge-transfer (CT) emission.[7] The observation of luminescence in these systems has played a key role in initiating experiments[8] directed toward elucidating their intramolecular and intermolecular excited-state decay processes. We now report the first examples of metal carbonyls which undergo radiative decay in room temperature fluid solution.

Results

a. **Electronic Absorption Spectra.** The low-spin d^6 $ClRe(CO)_3X$ (X = 5-Y-1,10-phenanthroline (Y = H, CH_3, Cl, Br, NO_2), 4,7-diphenyl-1,10-phenanthroline, 1,10-phenanthroline-5,6-dione, 2,2'-biquinoline) complexes exhibit absorption maxima in the optical region. A typical 298 and 77°K spectrum is shown in Figure 1 for X = 1,10-phenanthroline (1,10-phen), and spectral band maxima and molar extinction coefficients for each complex and the free ligands are detailed in Table I. Each of the complexes exhibits a lowest energy absorption maximum in the range 22,000–

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(8) (a) For Cr(III) important energy transfer experiments have aided in identification of the substitutionally reactive excited state; cf., for example, N. Sabbatini and V. Balzani, *J. Amer. Chem. Soc.*, **94**, 7587 (1972). (b) Solution luminescence from Ru(2,2'-bipy)²⁺ has led to its use as an aqueous solution triplet sensitizer: J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1800 (1971).
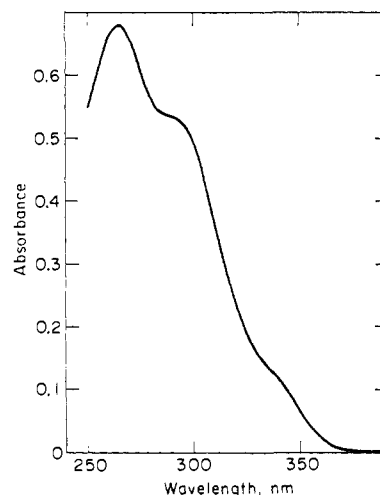
26,000 cm^{-1} with a molar extinction coefficient between $2-4 \times 10^3$ l. cm^{-1} mol^{-1}. The band appears to be composed of at least two components which are somewhat more well resolved at 77°K. The position of the band maximum is solvent sensitive shifting to higher energy in more polar media (*vide infra*), and the band is sensitive to the particular X; among the 5-Y-1,10-phenanthrolines the energy of the first band is in the order 5-CH_3– > 5-Cl– > 5-Br– > 5-NO_2. Each of the complexes also exhibits an intense (ϵ 25,000 l. cm^{-1} mol^{-1}) transition in the optical absorption spectrum which appears near the free ligand absorption. It is noteworthy that the maximum of the lowest absorption in $ClRe(CO)_3(2,2'$-biquinoline) is substantially lower than the complexes of 1,10-phenanthroline derivatives, and the 2,2'-biquinoline has the lowest free ligand absorption.

The electronic absorption spectrum of $ClRe(CO)_3$-$(py)_2$ is shown in Figure 2 and is seen to be very different from the $ClRe(CO)_3X$ complexes in that the lowest absorption band maxima are at substantially higher energy. The lowest energy absorption is a shoulder at 29,000 cm^{-1} with ϵ 1000 l. cm^{-1} mol^{-1}.

b. **Luminescence Phenomena.** The $ClRe(CO)_3X$ complexes all exhibit optical luminescence upon electronic excitation at 77°K in glassy solvents, and many of the complexes luminesce at room temperature in the solid state or in fluid solutions. A typical absorption–emission system is included in Figure 1, and emission maxima, lifetimes, and quantum yields are set out in Table II. The following points seem general:

Table II. Luminescence Characteristics for ClRe(CO)₃Xᵃ

X	Emission max, kcm⁻¹ 298°K	Emission max, kcm⁻¹ 77°K	Lifetime, sec × 10⁶ 298°K	Lifetime, sec × 10⁶ 77°K	$\phi \pm 15\%$ᶜ 298°K	$\phi \pm 15\%$ 77°K
1,10-Phenanthroline	17.33	18.94	0.3	9.6	0.036	0.33
2,2'-Bipyridyl		18.87	0.6	3.8		
5-Methyl-1,10-phenanthroline	17.01	18.83	≤0.65	5.0	0.03₀	0.33
4,7-Diphenyl-1,10-phenanthroline	17.24	18.18	0.4	11.25		
5-Chloro-1,10-phenanthroline	17.12	18.69	≤0.65	6.25		
5-Bromo-1,10-phenanthroline	17.12	18.69	≤0.65	7.6	0.02₀	0.20
5-Nitro-1,10-phenanthroline	b	18.28		11.8		0.03₃
1,10-Phenanthroline-5,6-dione	b	18.45		2.5		
2,2'-Biquinoline	b	14.58ᶜ				

ᵃ 77°K measurements in EPA; 298°K measurements in CH₂Cl₂, using a 1P21 PMT detector unless specified otherwise. ᵇ Luminescence at 298°K is not detectable from these complexes in solution. ᶜ RCA 7102 PMT detector, quantum yields in 298°K solutions measured in benzene solvent.
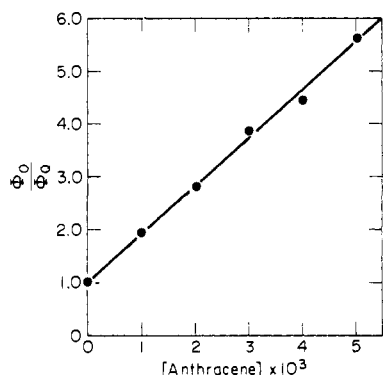
Figure 3. Stern–Volmer plot for anthracene quenching of ClRe-(CO)₃(5-Cl-1,10-phen) luminescence in degassed CH₂Cl₂ solution.

the room temperature solution luminescence is shorter lived, much less intense, and red-shifted compared to the 77°K phenomena, the emission is structureless, and lifetimes, quantum yields, and emission maxima are modestly affected by X. The diminished luminescence yields in solutions at 298°K are not accompanied by a marked increase in photoreactivity. The excitation spectra for the luminescence strongly resembles the absorption spectra of the complexes, especially in the region below 33,000 cm⁻¹. The emission spectra are independent of the excitation wavelength.

We have been unable to detect luminescence from the ClMn(CO)₃(1,10-phen) or the ClMn(CO)₃(5-Br-1,10-phen) analogs of the Re complexes. Additionally, the ClRe(CO)₃(py)₂ complex exhibits no measureable luminescence under any conditions.

As indicated above, the first absorption maximum in ClRe(CO)₃X is sensitive to solvent polarity. Data in Table II indicate that the emission maximum depends on the particular X, but the peculiar result is that the emission maximum typically moves ∼1500 cm⁻¹ to the blue upon cooling ClRe(CO)₃X to 77°K in EPA solution. Some solvent and environmental effects on both absorption and luminescence maxima are detailed in Table III. The rigid media (EPA at 77°K, pure solids, polyester resin) yield substantially higher energy emissions than for solutions at 298°K. Further, the rigid polyester resin medium yields more intense, longer lived emission compared to fluid solutions. The emission maxima in 298°K solutions do not shift with varying solvent polarity while the absorption maxima shift ∼1500 cm⁻¹.

The unusually large changes in emission maxima with

Table III. Summary of Environmental Effects on Absorption and Emission Maxima of ClRe(CO)₃X

X	Environment, T°K	First absorption max, kcm⁻¹	Emission max, kcm⁻¹($\tau \times$ 10⁶ sec),
1,10-Phenanthroline	CH₂Cl₂, 298°	26.53	17.33 (0.3)
	Polyester resin, 298°		18.52 (3.67)
	EPA, 77°		18.94 (9.6)
5-CH₃-1,10-phenanthroline	Benzene, 298°	25.65	17.00 (≤0.65)
	CH₂Cl₂, 298°	26.32	17.01
	CH₃OH, 298°	27.05	17.00
	Pure solid, 298°		18.42
	Polyester resin, 298°		18.48 (3.5)
	EPA, 77°		18.83 (5.0)
5-Br-1,10-phenanthroline	Benzene, 298°	25.32	17.15 (≤0.65)
	CH₂Cl₂, 298°	25.84	17.12
	CH₃OH, 298°	26.88	17.04
	Pure solid, 298°		17.83
	Polyester resin, 298°		18.32 (2.2)
	EPA, 77°		18.69 (7.6)
5-Cl-1,10-phenanthroline	CH₂Cl₂, 298°	25.91	17.12
	Pure solid, 298°		17.99
	EPA, 77°		18.69 (6.25)

differing environment led us to question the stability of the ClRe(CO)₃X complexes. Three independent criteria rule out sample degradation to account for the observations: (1) ir spectra in the CO stretching region and uv–visible spectra are constant in time; (2) absorption spectral shifts in EPA as a function of temperature are reversible and take place without isosbestic points; (3) temperature effects on luminescence in EPA are reversible.

c. Quenching Phenomena. Oxygen, anthracene, and *trans*-stilbene are observed to quench the room temperature luminescence of the ClRe(CO)₃X complexes. Anthracene (triplet energy (E_T) = 42 kcal/mol)[9] and *trans*-stilbene (E_T = 50 kcal/mol)[10] obey Stern–Volmer kinetics[9] for the quenching as evidenced by linear plots of ϕ_0/ϕ_Q against quencher concentration as shown in Figure 3 for anthracene. The slope of the Stern–Volmer plot ($k_q\tau$) is 9.15 × 10² M^{-1} for anthracene and 9.03 × 10¹ M^{-1} for *trans*-stilbene using ClRe(CO)₃(5-Cl-1,10-phen) as the donor.

Accompanying the quenching of ClRe(CO)₃X luminescence by *trans*-stilbene we find *trans* → *cis*-stilbene isomerization. The ClRe(CO)₃X sensitized *trans* →

(9) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967.
(10) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).

cis-stilbene isomerization quantum yields upon excitation at 366 nm for three donors are set out in Table IV. The intersystem crossing efficiency for benzo-

Table IV. ClRe(CO)₃X Sensitized Stilbene Isomerization[a]

X	$\phi_{trans \to cis} \pm 10\%$
5-CH₃-1,10-phenanthroline	0.62
5-Cl-1,10-phenanthroline	0.65
5-Br-1,10-phenanthroline	0.52

[a] Benzene solutions at 25°.

phenone is unity.[9] Thus, a comparison of the benzophenone triplet sensitized *trans → cis*-stilbene isomerization[10] quantum yields with the yields for ClRe(CO)₃X will give an absolute efficiency for triplet production in ClRe(CO)₃X assuming that the quenching of the ClRe-(CO)₃X emission is accompanied by production of the free triplet of the olefin. The intersystem crossing efficiency in ClRe(CO)₃X is 1.0 ± 10% assuming the benzophenone sensitized *trans → cis*-stilbene isomerization to be 0.60.[10] Finally, with respect to stilbene isomerization we note that the ClRe(CO)₃(4,7-Ph₂-1,10-phen) sensitization produces a photostationary state which contains at least 97.0% *cis*-stilbene.

Discussion

The results outlined above lead to some important conclusions regarding the nature of the lowest excited states in the ClRe(CO)₃X complexes. We begin by assigning the electronic absorption spectrum followed by consideration of the excited-state decay paths in the complexes.

The assignment of the low energy region of the absorption spectrum is complicated by the possibility of both LF[11] and CT absorptions involving X, CO, and Cl.[1,2] Strong support, though, is found for the assignment of the lowest absorption system as principally a Re → X π* CT absorption. First, the fact that ClRe(CO)₃(py)₂ exhibits no absorption maxima below 29,000 cm⁻¹ rules out an LF assignment since this complex has the same donor atoms as in the ClRe-(CO)₃X complexes, and it is known that 1,10-phenanthroline and pyridine occupy a comparable position in the spectrochemical series with 1,10-phenanthroline perhaps actually a little higher.[12] The substantially lower energy absorption for X = 2,2′-biquinoline compared to X = 1,10-phenanthroline is consistent with the lower energy of the π → π* intraligand absorption for the 2,2′-biquinoline, and an Re → X π* CT transition should, then, be lowered. The substituent effect in the 1,10-phenanthrolines where more electron withdrawing substituents yield lower energy absorptions is consistent with the Re → X π* CT direction of CT. The solvent effect on the first absorption band in ClRe(CO)₃X is like that found for the M → L π* CT absorption in M(CO)₄L (M = Cr, Mo, W; L = 1,10-phenanthroline, 2,2′-bipyridine) which also have the low-spin d⁶ electronic configuration.[13] The M → L π* CT in M-

(CO)₄L also corresponds to the lowest energy absorption[13] as we find in ClRe(CO)₃X. The M(CO)₄L complexes also exhibit an intense absorption near the free ligand absorption which is assigned as an intraligand absorption. Analogously, we assign the corresponding band in ClRe(CO)₃X as an intraligand absorption. The LF transitions are expected to appear at no less than 29,000 cm⁻¹ based upon the ClRe(CO)₃(py)₂ spectra, but this region is obscured in ClRe(CO)₃X spectra by the onset of intraligand absorption.

The luminescence characteristics point to an association of the emission with the Re → X π* CT absorption band, and the lack of emission from the first row Mn analogs, the luminescence lifetimes, and the quenching experiments are consistent with a radiative transition which is, at least partially, triplet → singlet in character. The lack of emission from Cr(CO)₅-(n-electron donor) where LF emission is expected[4a] and very weak emission from Cr(CO)₄(1,10-phen) where CT emission is expected,[14] while in each case the third-row W complexes emit, is attributed in part to the smaller spin-orbital coupling of the first-row metals. The larger spin–orbital coupling associated with Re(I) compared to Mn(I) likewise will play a large role in relaxing the spin forbiddenness of a triplet–singlet transition. The emission lifetimes for ClRe(CO)₃X are similar to those for other heavy metal complexes where spin-forbidden emission obtains.[4b,14,15] The CT character of the emission is substantial, LF and intraligand emission being ruled out, respectively, by the lack of detectable emission from ClRe(CO)₃(py)₂ and the lack of vibrational structure[16] and the energetic discrepancy of the ClRe(CO)₃X emission compared to X emission at low temperatures. The dependence of the emission maximum on X which crudely parallels the absorption phenomena and the unusually large environmental effects on ClRe(CO)₃X emission support a CT assignment. Curiously, the luminescence maximum in solutions at 298°K are constant while the first absorption maximum is shifting ~1500 cm⁻¹ depending on the solvent. This apparent uncoupling of the absorption and emission phenomena may be due to the fact that the absorption is principally a spin-allowed transition while the emission is principally spin forbidden, and, additionally, while the absorption maxima clearly shift it is not equally clear that the absorption onset shifts by the same amount. Further, there is no reason to assume that the solvent cannot change the shape of the excited-state potential well without substantially affecting the potential minimum. The strong dependence of the emission maxima upon environmental rigidity leads to orange-red emission in fluid media and yellow-green emission in rigid media. We call this unique effect a *rigidochromic* effect, (change in color depending on environmental rigidity) and in particular, a *luminescence rigidochromic* effect is observed for ClRe(CO)₃X complexes. The detailed

(11) Reference 2b puts the first LF absorption maximum for Re-(CO)₆⁺ at 26,850 cm⁻¹. Substitution of three CO's by Cl⁻ and two nitrogen donors should substantially lower the average LF strength to yield lower lying LF states for ClRe(CO)₃X compared to Re(CO)₆⁺.

(12) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 243.

(13) H. Saito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, 41, 359, 863 (1968).

(14) Emission yields for M(CO)₄L (M = Cr, Mo, W; L = 1,10-phenanthroline and related ligands)⁴ have been measured: M. Wrighton and D. L. Morse, submitted for publication.

(15) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 70, 199 (1970).

(16) We have been able to easily observe the vibrational structure of X phosphorescence at 77°K in EPA under the same conditions where we obtain ClRe(CO)₃X emission.

origin of the effect is not understood and is now under investigation.

The low temperature luminescence quantum yields in EPA are substantial and some variations are noted. For X = 5-H-, 5-CH$_3$-, 5-Br-, and 5-NO$_2$-1,10-phenanthroline the radiative decay rate constants, k_r, are 3.44 × 10^4, 6.60 × 10^4, 2.63 × 10^4, and 0.28 × 10^4 sec^{-1}, respectively, while the nonradiative decay rate constants are 0.70 × 10^5, 1.34 × 10^5, 1.05 × 10^5, and 0.82 × 10^5 sec^{-1}. Thus, the large deviation in emission efficiency in the 5-NO$_2$- is due mainly to a decrease in k_r since k_{nr} is essentially constant among the complexes. This result is similar to that found for M(CO)$_4$L complexes[14] and is consistent with the geometrical similarity of the ClRe(CO)$_3$X complexes and with the small variation of the emission maximum leading to relatively small changes in k_{nr} which could be ascribed solely to differences in the ground–excited-state energy gap.[17]

Room temperature luminescence lifetimes and quantum yields in fluid solutions are about 1 order of magnitude smaller than those at 77°K, consistent with a relative increase in the rate of nonradiative decay. The lack of photoreactions in fluid solutions reveals that the electronic excited-state ultimately achieved upon excitation is neither reactive itself nor does it channel electronic excitation energy into production of a hot-ground-state molecule which can yield CO substitution. The similarity of the excitation and absorption spectra lead to the prediction that the reactions from upper excited states will have small absolute quantum efficiency.

While the large degree of spin–orbital coupling in a third-row metal is enough to preclude discrete singlets and triplets, the room temperature quenching of ClRe(CO)$_3$X luminescence is wholly consistent with the notion that these complexes can behave as normal triplet donors. Energetically, the triplet level of anthracene ($E_T \cong 42$ kcal/mol) is well below the ClRe(CO)$_3$(1,10-phen) state, and anthracene quenches at nearly a diffusion controlled rate assuming $\tau \cong 10^{-7}$ sec. The trans-stilbene triplet level ($E_T \approx 50$ kcal/mol) is only isoenergetic with the ClRe(CO)$_3$(1,10-phen), and trans-stilbene quenches much more slowly as expected for quenching by triplet–triplet collisional energy transfer. The singlet states of anthracene and trans-stilbene are too high in energy to play a role in the quenching activity. That the triplet excited state of trans-stilbene is produced is evidenced by the ClRe(CO)$_3$X sensitized formation of cis-stilbene, i.e., movement away from the thermodynamic ratio of the stilbenes.[18] The lack of any disappearance of ClRe(CO)$_3$X in the sensitization experiments rules out coordination of the stilbene. Further, the large amount of the cis-stilbene at the photostationary state achieved by ClRe(CO)$_3$X sensitization is consistent with triplet–triplet transfer from a donor of energy less than the cis-stilbene triplet ($E_T \cong 57$ kcal/mol).[10] Finally, the fact that the benzophenone and the ClRe(CO)$_3$X sensitized trans → cis-stilbene yields are the same is consistent with unit efficiency for triplet production from the ClRe(CO)$_3$X donors.

(17) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

(18) G. Fischer, K. A. Muszkat, and E. Fischer, J. Chem. Soc. B, 156 (1968).

Experimental Section

Preparation of ClRe(CO)$_3$X. The ligands (X) are commercially available from K & K Chemical Co. or Aldrich Chemical Co. The ClRe(CO)$_3$(py)$_2$ was synthesized[19,20] by heating ClRe(CO)$_5$ (obtained from Pressure Chemical Co.) to 60° in benzene solution in the presence of pyridine. The solution was concentrated by rotary evaporation and addition of n-pentane precipitated the off-white crystalline product. Purification was achieved by recrystallization from CH$_2$Cl$_2$ by addition of n-pentane. A satisfactory C and N analysis was obtained by Alfred Bernhardt. Anal. Calcd: C, 33.62; N, 6.03. Found: C, 33.75; N, 6.13. Ir bands in CH$_2$Cl$_2$ solution were found at 2025, 1920, and 1885 cm^{-1} in the CO stretching region in excellent agreement with the previously reported values.[19]

Heating of ClM(CO)$_5$ (M = Mn, Tc, Re) in the presence of X is known to result in the formation of ClM(CO)$_3$X,[20] and literature procedures were followed with modest variation. We will describe the synthesis of ClRe(CO)$_3$(5-CH$_3$-1,10-phen) which is representative of a typical ClRe(CO)$_3$X preparation. The 5-methyl-1,10-phenanthroline and ClRe(CO)$_5$ were dissolved in a 2:1 mole ratio in benzene and heated to 60° for several hours. Concentration of the solution by rotary evaporation followed by addition of n-pentane resulted in precipitation of the yellow solid ClRe(CO)$_3$-(5-CH$_3$-1,10-phen). Purification was achieved by recrystallization from CH$_2$Cl$_2$ by addition of n-pentane. A C, N, H, and Cl analysis was obtained from Alfred Bernhardt and found to be satisfactory. Anal. Calcd: C, 37.1; H, 1.93; N, 5.41; Cl, 6.84. Found: C, 38.3; H, 2.37; N, 5.56; Cl, 8.09. A C, H, and N analysis for ClRe(CO)$_3$(5-Cl-1,10-phen) proved satisfactory. Calcd: C, 33.40; H, 1.30; N, 5.30. Found: C, 32.53; H, 1.03; N, 6.27. Consistent with having the same CO arrangement as in the ClRe(CO)$_3$(py)$_2$, the ClRe(CO)$_3$X have a similar infrared spectrum in the CO stretching region: X = 1,10-phenanthroline 2015 (s), 1912 (m), 1890 (m) cm^{-1}; 5-CH$_3$-1,10-phenanthroline 2015 (s), 1912 (m), 1887 (m) cm^{-1}; 5-Cl-1,10-phenanthroline 2015 (s), 1910 (m), 1888 (m) cm^{-1}; 5-Br-1,10-phenanthroline 2015 (s), 1915 (m), 1893 (m) cm^{-1}; 1,10-phenanthroline-5,6-dione 2015 (s), 1922 (m), 1899 (m) cm^{-1}. Ir spectra were measured in CH$_2$Cl$_2$ solution. The ClRe(CO)$_3$X complexes are typically very thermally and light insensitive. Incidentally, irradiation of ClRe(CO)$_5$ in the presence of X yields the ClRe(CO)$_3$X complexes at room temperature.

Spectra. Infrared spectral measurements were made using a Perkin-Elmer 237 spectrometer. All uv–visible absorption spectra were obtained using a Cary 17 spectrophotometer. Measurements at 77°K were carried out using a liquid N$_2$ dewar having optical quality quartz flats for the windows. Spectral measurements at 77°K were carried out using EPA obtained from MC & B Chemical Co. as the solvent. All emission measurements were made using an Aminco-Bowman spectrophotofluorometer. The emission instrument was equipped with either a 1P21 PMT for most samples or a Dry Ice cooled RCA 7201 PMT for detection of the ClRe(CO)$_3$-2,2'-biquinoline) emission. All emission maxima cited in this paper and the emission spectra shown in Figure 1 are uncorrected. The polyester resin was from Fibre-Glass Evercoat Co., Inc. The resin was supplied as a very viscous liquid in which the ClRe(CO)$_3$X complexes are soluble. Emission spectral maxima were found to be very similar to fluid solution maxima (CH$_2$Cl$_2$, benzene, CH$_3$OH solution), but after addition of the hardening agent (methyl ethyl-ketone peroxide) the resin hardened substance yielded emission maxima substantially blue-shifted, and more intense and longer lived emission. Samples were hardened for typically 24 hr at room temperature and no decomposition of ClRe(CO)$_3$X was noted.

Luminescence Quantum Yields. Absolute luminescence quantum yields for ClRe(CO)$_3$X at 77°K in EPA were measured relative to fluorescein in 298°K aqueous carbonate-bicarbonate buffer of pH 9.6 having a luminescence yield of 0.85.[17] Luminescence yields of ClRe(CO)$_3$X in 298°K benzene solution were determined relative to rhodamine B in ethanol with a luminescence yield of

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0.69.[17] Care was taken to match the optical density of the sample and the standard under the conditions of the measurement.

Luminescence Lifetimes. Emission lifetimes were measured using a TRW Model 75A decay time fluorometer equipped with a Xenon Corp. Model 437 Nanopulser exciting source. Appropriate filters were used on both the exciting and emission side to minimize scattered light from the excitation pulse. The RCA 931A photomultiplier tube (PMT) was powered by a Kepco Model ABC 2500 regulated high voltage power supply. The output of the PMT was monitored with a Tektronix 453 oscilloscope and recorded with a Polaroid camera. Plots of log (luminescence intensity) against time were linear in each case. Lifetimes at 298°K determined in degassed solution were difficult to obtain due to the weak emission intensity, spectral position, and the relatively long excitation pulse duration.

Quenching of ClRe(CO)$_3$X Luminescence. Solutions (in 13 ×

100 mm test tubes) of the ClRe(CO)$_3$X and the quencher (anthracene or *trans*-stilbene) were degassed by at least three freeze–pump–thaw cycles and the relative luminescence quantum yields determined using the Aminco-Bowman emission spectrophotometer. To determine the quantum yields for the ClRe(CO)$_3$X sensitized *trans* → *cis*-stilbene reaction the samples were prepared such that all of the ClRe(CO)$_3$X luminescence was quenched. The tubes were irradiated in parallel with actinometry tubes containing benzophenone (0.05 M) and *trans*-stilbene (~0.05 M) using a merry-go-round[21] equipped with a 550-W Hanovia lamp filtered with Corning filter no. 7–83 to isolate the 366-nm region of the Hg lamp output.

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Kinetics of Olefin Oxidation by Tetrachloropalladate in Aqueous Solution

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Contribution from the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, Moscow, USSR. Received June 4, 1973

Abstract: Different possible forms of the kinetic equation for the reaction between PdCl$_4{}^{2-}$ and olefin in aqueous solution were analyzed. It was concluded that over a wide range of temperature, ionic strength, and concentrations of PdCl$_4{}^{2-}$, Cl$^-$, and H$_3$O$^+$ the kinetics of olefin oxidation are described by a two-term equation (including a quadratic term in [PdCl$_4{}^{2-}$]) rather than by a one-term equation, the latter being valid only for low Pd(II) concentration. The validity of the two-term equation extends over a wide range of variation of numerical values of the equilibrium constants of the π-complex formation used in calculations of the reaction rates. A comparison of the rates of ethylene oxidation in solutions of identical initial composition observed by the authors and by Henry leads to the conclusion that diffusion limitation seems to be appreciable in Henry's studies of the gaseous ethylene uptake by PdCl$_4{}^{2-}$ solutions.

The kinetics of olefin oxidation by palladium chloride in aqueous solutions have been studied by a number of authors.[1–8] It has been shown in our laboratory[6,7] that the rate of reaction between PdCl$_4{}^{2-}$ and olefin in solution obeys the equation

$$w = k_\mathrm{I}\frac{[\mathrm{PdCl_4{}^{2-}}][\mathrm{C}_n\mathrm{H}_{2n}]}{[\mathrm{Cl^-}]^2[\mathrm{H_3O^+}]} + k_\mathrm{II}\frac{[\mathrm{PdCl_4{}^{2-}}]^2[\mathrm{C}_n\mathrm{H}_{2n}]}{[\mathrm{Cl^-}]^3[\mathrm{H_3O^+}]} \quad (1)$$

The kinetic data related to the range of concentration of Pd(II) (0.01–0.2 M), temperature (25°), and ionic strength (3 M) have shown[6] that initial data are described better by eq 1 than by eq 2

$$W = k\frac{[\mathrm{PdCl_4{}^{2-}}][\mathrm{C}_n\mathrm{H}_{2n}]}{[\mathrm{Cl^-}]^2[\mathrm{H_3O^+}]} \quad (2)$$

The difference between eq 1 and more complicated equations is (as it follows from the regression analysis)

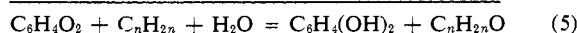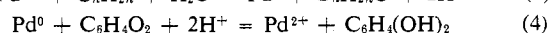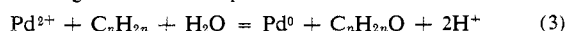within the scattering of kinetic experimental data (10–15%).

We report in this paper the kinetic data confirming the validity of eq 1 at all values of Pd(II), Cl$^-$, and H$_3$O$^+$ concentrations, ionic strength, and temperature where the PdCl$_4{}^{2-}$ form prevails.

Experimental Section

All inorganic salts were reagent grade. PdCl$_2$ ("pure" grade) was purified by reduction in aqueous solution of sodium formate at 60° and pH 8–9, followed by thorough washing with water and HCl and dissolving in concentrated HCl and H$_2$O$_2$. PdCl$_2$ obtained from this solution was dried at 300–350° in dry HCl atmosphere. *Anal.* Calcd for PdCl$_2$: Pd, 60.0; Cl, 40.0. Found: Pd, 59.9; Cl, 39.87. The purification of other chemicals and the procedure of solution preparation have been described previously.[7]

The kinetics of reaction between Pd(II) and dissolved olefin were studied in the presence of *p*-benzoquinone by measuring the emf of the following cell, one electrode of which was a quinone-hydroquinone (Q, QH$_2$) electrode in the reactant medium, Pt|Q,QH$_2$,Pd-(II), HCl, LiClO$_4$, olefin|Pd(II), HCl, LiClO$_4$, Q, QH$_2$|Pt.

The following reactions take place in the emf cell

$$\mathrm{Pd^{2+}} + \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{H_2O} = \mathrm{Pd^0} + \mathrm{C}_n\mathrm{H}_{2n}\mathrm{O} + 2\mathrm{H^+} \quad (3)$$

$$\mathrm{Pd^0} + \mathrm{C_6H_4O_2} + 2\mathrm{H^+} = \mathrm{Pd^{2+}} + \mathrm{C_6H_4(OH)_2} \quad (4)$$

$$\mathrm{C_6H_4O_2} + \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{H_2O} = \mathrm{C_6H_4(OH)_2} + \mathrm{C}_n\mathrm{H}_{2n}\mathrm{O} \quad (5)$$

As we have found earlier[9] this reaction proceeds quantitatively

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