(br s, 1 H); ^{19}F NMR (acetone-d_6/CFCl$_3$) δ −143.0 (dd, J = 21.9, 7.9 Hz, 2 F), −158.6 (t, J = 20.3 Hz, 1 F), −164.0 (ddd, J = 21.9, 20.3, 7.9 Hz, 2 F); IR (neat) 1730 ($\nu_{C=O}$) cm^{-1}.

2-(Pentafluorophenyl)butanal (7a): ^{1}H NMR (CDCl$_3$) δ 0.98 (t, J = 7.4 Hz, 3 H), 1.85 (m, 1 H), 2.29 (m, 1 H), 3.78 (dd, J = 9.8, 5.4 Hz, 1 H), 9.75 (t, J = 2.2 Hz, 1 H); ^{19}F NMR (acetone-d_6/CFCl$_3$) δ −141.5 (dd, J = 21.5, 7.0 Hz, 2 F) −156.6 (t, J = 20.4 Hz, 1 F), −163.4 (ddd, J = 21.5, 20.4, 7.0 Hz, 2 F); IR (neat) 1730 ($\nu_{C=O}$) cm^{-1}.

***n*-Propylpentafluorobenzene (8a)**: ^{1}H NMR (CDCl$_3$) δ 0.93 (t, J = 7.2 Hz, 3 H), 1.60 (sextet, J = 7.2 Hz, 2 H), 2.65 (m, 2 H); ^{19}F NMR (acetone-d_6/CFCl$_3$) δ −144.9 (dd, J = 21.8, 7.4 Hz, 2 F), −159.7 (t, J = 20.3 Hz, 1 F), −164.4 (ddd, J = 21.8, 20.3, 7.4 Hz, 2 F); IR (neat) 2980, 2930, 2870, 1515, 1500, 1120, 1105, 1000, 970, 950 cm^{-1}; MS 210 (20, M$^+$), 181 (100).

Hydroformylation of Vinyl Fluoride (VF). Reactions were run in a manner similar to that for TFP with 20 mmol of substrate and Rh$_4$(CO)$_{12}$ (0.01 mmol), HRh(CO)(PPh$_3$)$_3$ (0.04 mmol), Ru$_3$(CO)$_{12}$ (0.2 mmol), and Co$_2$(CO)$_8$ (0.2 mmol) as catalysts at 80 °C (68 atm) (CO/H$_2$ = 1) for the rhodium and ruthenium catalysts and at 100 °C (110 atm) (CO/H$_2$ = 1) for the cobalt catalyst in toluene for 18 h. The sole product, 2-fluoropropanal (2-FPA), was obtained by distillations as colorless liquid. The yield of 2-FPA was the following: Rh$_4$(CO)$_{12}$, 81%; HRh(CO)(PPh$_3$)$_3$, 52%; Ru$_3$(CO)$_{12}$, 46%; Co$_2$(CO)$_8$, 30%.

2-Fluoropropanal (2-FPA): bp 56–56.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.48 (dd, J = 23.8, 7.0 Hz, 3 H), 4.90 (dq, J = 48.7, 7.0 Hz, 1 H), 9.78 (d, J = 5.9 Hz, 1 H); ^{19}F NMR (CDCl$_3$/CFCl$_3$) δ −192.87 (dqd, J = 48.7, 23.8, 5.9 Hz); IR (neat) 1724 ($\nu_{C=O}$) cm^{-1}.

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Photochemistry of the Orthometalated *cis*-Bis[2-(2-thienyl)pyridine]platinum(II) Complex in Halocarbon Solvents

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Abstract: The photochemical and luminescence behavior of the orthometalated Pt(thpy)$_2$ complex, where thpy$^-$ is the ortho-C-deprotonated form of 2-(2-thienyl)pyridine, has been studied under a variety of experimental conditions, and the mechanisms of the excited-state reactions and of the subsequent thermal processes are discussed. In degassed CH$_3$CN the complex is not photosensitive and exhibits luminescence from the lowest triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state with Φ_{em} = 0.26 and τ = 2.4 μs. In CH$_2$Cl$_2$, CHCl$_3$, or CH$_3$CN/CH$_2$Cl$_2$ solvents, the complex maintains its luminescent properties and undergoes a photooxidative addition reaction with formation of Pt(thpy)$_2$(Cl)(R) (R = CH$_2$Cl or CHCl$_2$) as the sole observed product. In the mixed solvent, the quantum yield of the photoreaction increases with increasing CH$_2$Cl$_2$ concentration. In neat CH$_2$Cl$_2$, the quantum yield of the photoreaction is 0.30 and 0.10 for 313- and 430-nm excitation, respectively. In CH$_2$Cl$_2$, complete quenching of the luminescent ^{3}MLCT excited state by anthracene via an energy-transfer mechanism is accompanied by only partial quenching of the photoreaction. By contrast, oxygen is a better quencher for the photoreaction than for the luminescence emission. In both cases the fraction of quenched reaction depends on the excitation wavelength. These and other results are interpreted on the basis of a mechanism involving generation of Pt(thpy)$_2$Cl and CH$_2$Cl radicals via (i) a charge transfer to solvent (CTTS) excited state, populated from the intraligand (IL) and metal-to-ligand charge-transfer (MLCT) states obtained by light absorption, and (ii) the thermally relaxed ^{3}MLCT luminescent level, through conversion to CTTS or bimolecular reaction with CH$_2$Cl$_2$. The primary radicals are then involved in a chain mechanism of the type previously discussed for other oxidative addition reactions, with an average chain length of about 40.

There is currently a growing interest in the study of the photochemical and photophysical behavior of orthometalated transition-metal complexes.[4-11] Such investigations are, on one side, a logic extension of the numerous and detailed studies carried out in the last decade on transition-metal complexes containing polypyridine-type ligands;[12-15] on another side, they represent one of the expected developments of organometallic chemistry, a field that has so far contributed a relatively small number of studies aimed at the characterization of excited-state reactivity and/or luminescence.[16-18] The main goals of the photochemical and photophysical investigations on organometallic transition-metal complexes are to discover and characterize new molecules that can play the role of light absorption and/or light emission sen-

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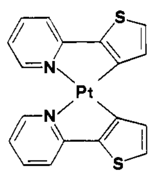

Figure 1. Structural formula of Pt(thpy)$_2$.

sitizers[19] and to develop and elucidate new catalytic processes.[16-18]

We have found[9,20] recently that the orthometalated Pt(II) complexes Pt(phpy)$_2$ and Pt(thpy)$_2$, where phpy$^-$ and thpy$^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine, are photosensitive in several organic solvents, giving rise to oxidative addition reactions that lead to the formation of new luminescent Pt(IV) complexes. The Pt(thpy)$_2$ complex (Figure 1) is particularly interesting since it is able to emit a relatively strong luminescence in fluid solution at room temperature,[8] i.e. under the experimental conditions used for photochemical studies. This rather unusual property offers the opportunity to try to elucidate the excited-state mechanism of the photochemical reaction via comparative photochemical and luminescence quenching experiments. This has prompted us to examine the mechanism of the photochemical behavior of Pt(thpy)$_2$ in some detail using different solvents, different excitation wavelengths, and suitable quenchers of the luminescent excited state. An important investigation on the mechanism of photooxidative addition of a Pt(II) organometallic complex has recently been reported by Hill and Puddephatt.[21]

Experimental Section

Materials. *cis*-Bis[2-(2-thienyl)pyridine]platinum(II) (Figure 1), hereafter simply indicated by Pt(thpy)$_2$, was prepared and purified following a procedure previously described.[20,22] All the other chemicals were of the best commercial grade.

Apparatus. For the photochemical experiments, radiations of 313 or 430 nm were obtained as previously described.[23] The intensity of the incident light, measured by means of the ferric oxalate actinometer,[24] was of the order of 10^{-7} *Nhν*/min. The concentration of the complex was usually of the order of 1.0×10^{-4} M. The fraction of absorbed light was calculated from the optical density of the irradiated solutions. The reaction cells were spectrophotometric cells (thickness 1 cm; capacity 3 mL). Unless otherwise noted, the solutions were degassed by repeated freeze-pump-thaw cycles. The absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer and the emission spectra recorded with a Perkin-Elmer LS5 spectrofluorimeter equipped with a R928 Hamamatsu phototube. Emission quantum yields were measured with the optically diluted method[25] by using Ru(bpy)$_3^{2+}$ in aerated solution as a standard ($\Phi_{em} = 0.028$).[26] Emission lifetimes were measured with a JK system 2000 Neodymium Yag DLPY 4 laser (third harmonic; pulse half-width 20 ns), equipped with a Tektronix transient digitizer.

Procedures. All the experiments were carried out at room temperature (~20 °C). The thermal stability of the solution was controlled in parallel runs. The progress of the photoreaction was monitored by changes in absorbance in the maximum of the band in the visible. For quantum yield determination, the complex concentration was such to have complete light absorption and the photoreaction was carried out up to the disappearance of no more than 20% of the initial concentration, unless otherwise noted. For the luminescence experiments, the excitation wavelength was 420 nm and the emission was monitored at 580 nm. For the emission decay measurements, the excitation wavelength was 355 nm and the emission was monitored at 580 nm. In the quenching experiments by anthracene, the maximum concentration of the quencher used was 1.2×10^{-3} M. At 430 nm, the exciting light was completely absorbed by Pt(thpy)$_2$. At 313 nm, 36% of the exciting light was absorbed by anthracene at the beginning of the experiment and appropriate corrections were performed in order to obtain the photoreaction quantum yield.

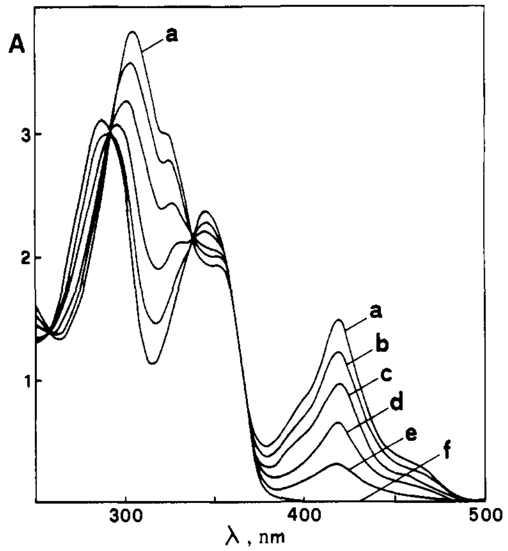

Figure 2. Spectral changes for a Pt(thpy)$_2$ 1.4×10^{-4} M solution in deaerated CH$_2$Cl$_2$ on irradiation with 313-nm light. The irradiation times are 0 min (a), 2 min (b), 4 min (c), 6 min (d), 8 min (e), and 10 min (f).

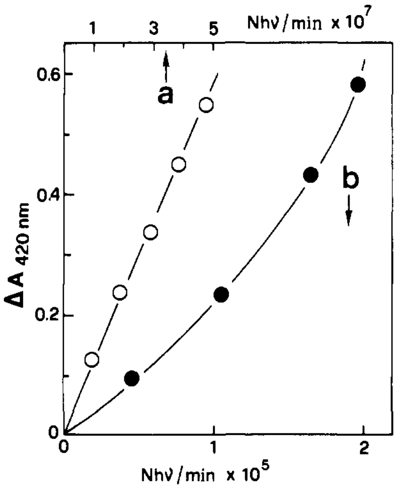

Figure 3. Absorption changes at 420 nm for a Pt(thpy)$_2$ 1.4×10^{-4} M solution in CH$_2$Cl$_2$ on 313-nm irradiation: deaerated solution (a); aerated solution (b).

Results

The absorption spectrum of Pt(thpy)$_2$ (Figure 2, curve a) has been previously reported.[8] The lowest energy absorption band has been assigned to a MLCT transition. The shape and intensity of the absorption spectrum was found to be slightly solvent dependent, with a red shift on going from CH$_3$CN to CH$_2$Cl$_2$ of ~600 and ~300 cm^{-1} for the high-intensity UV and visible bands, respectively. In the UV region, this was also accompanied by an increase in the extinction coefficient of the order of 10%. With CHCl$_3$, slightly larger variations were observed in both the wavelengths of absorption maxima and the extinction coefficients. Several maxima were found in the difference spectra of CH$_3$CN and CH$_2$Cl$_2$ or CHCl$_3$ solutions.

In degassed CH$_2$Cl$_2$ solution, at each one of the excitation wavelengths, irradiation caused the disappearance of the MLCT band and other spectral changes with clean isosbestic points[20] (Figure 2). At the end of the photoreaction, only one species was present, which has been identified[20] by elemental analysis and NMR spectroscopy as the addition product Pt(thpy)$_2$(CH$_2$Cl)Cl. The concentration of the reacting complex decreased linearly with the number of absorbed einsteins (Figure 3a) up to completion

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Table I. Photochemical and Luminescence Results for $Pt(thpy)_2$ under Various Experimental Conditions

	photoreaction: $\Phi_r{}^a$		luminescence	
solution	313 nm	430 nm	$\Phi_{em}{}^b$	τ,^{c} μs
AN, degassed	$<5 \times 10^{-5}$	$<5 \times 10^{-5}$	0.26^d	2.4
AN, 6.2×10^{-2} M CH_2Cl_2, degassed	$\sim 5 \times 10^{-4}$		0.25	2.4
AN, 1.2 M CH_2Cl_2, degassed	2.0×10^{-2}	1.0×10^{-3}	0.27	2.4
AN, 7.5 M CH_2Cl_2, degassed	0.15	5.0×10^{-2}	0.24^e	2.8
CH_2Cl_2, degassed	0.30	0.10	0.30	3.0
CH_2Cl_2, aerated	$\sim 5 \times 10^{-3}$		1.7×10^{-2}	0.2
$CHCl_3$, degassed	~ 6			3.0
$CHCl_3$, aerated	$\sim 5 \times 10^{-2}$			0.2
CH_2Cl_2, 1.2×10^{-3} M anthracene, degassed	0.20	2.0×10^{-2}	$8 \times 10^{-3\,f}$	0.08^f

^{a}Estimated error ±10%. ^{b}Excitation in the visible MLCT band; estimated error ±20%. ^{c}Excitation at 355 nm; estimated error ±10%. ^{d}A value of 0.27 has been obtained for excitation in the tail of the UV band (λ = 372 nm). ^{e}A value of 0.22 has been obtained for excitation in the tail of the UV band (λ = 370 nm). ^{f}Extrapolated value; see Figure 5.

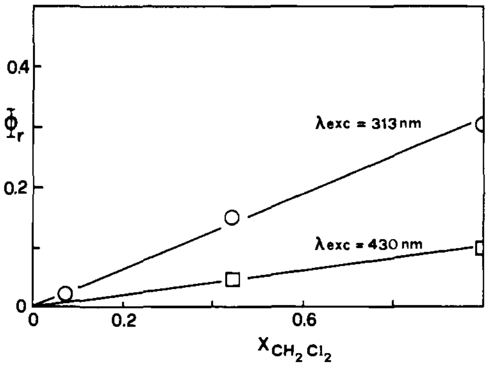

Figure 4. Variation in the quantum yield of the $Pt(thpy)_2$ photoreaction in CH_3CN/CH_2Cl_2 mixed solvents as a function of the CH_2Cl_2 molar fraction.

of the photoreaction. No postphotochemical effect was observed. The quantum yield of reactant disappearance was found to be wavelength dependent, as shown in Table I.

In deaerated CH_3CN solutions, no photochemical reaction was observed ($\Phi < 5 \times 10^{-5}$), but in degassed CH_3CN/CH_2Cl_2 mixed solvents, a photoreaction qualitatively identical with that found in neat CH_2Cl_2 was observed. The effect of CH_2Cl_2 concentration on the photochemical quantum yield was studied in the range 6.0 $\times 10^{-2}$–7.5 M. As one can see from Figure 4, the quantum yield increases linearly with increasing CH_2Cl_2 molar fraction. In all the experiments carried out in CH_3CN/CH_2Cl_2 mixtures, the concentration of the reacting complex increases linearly with increasing number of absorbed einsteins.

Irradiation of degassed $CHCl_3$ solutions caused spectral changes analogous to those observed in CH_2Cl_2, with formation of only one species, identified as the addition product $Pt(thpy)_2(CHCl_2)Cl$.[20] In this solvent the initial quantum yield was about 6 upon 313-nm excitation, and after photochemical initiation, the reaction proceeded for some time even in the dark.

Linear plots like that of Figure 3a with reproducible quantum yields can only be obtained if the solutions are rigorously degassed.

Irradiation of the complex at 313 nm in aerated CH_2Cl_2 or $CHCl_3$ solutions caused again the complete disappearance of the absorption in the visible and other spectral changes similar to, but not identical with, those observed in deaerated solutions. The quantum yield of reactant disappearance was much smaller than in deaerated solution (Table I) and increased with irradiation time (Figure 3b). The quenching effect of oxygen on the photochemical reaction was larger for $CHCl_3$ than for CH_2Cl_2 solutions (Table I). The photochemical reaction with CCl_4 could not be examined since an appreciable thermal reaction occurred upon mixing the reactants in the dark.

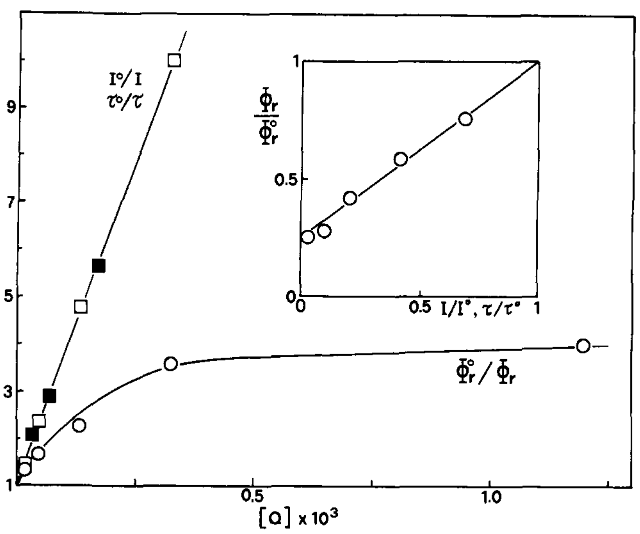

Figure 5. Stern–Volmer plots for the quenching of emission intensity (□), emission lifetime (■), and photoreaction quantum yield (○). The inset shows a plot of $\Phi_r/\Phi_r{}^0$ vs I/I^0 or τ/τ^0 (for more details see the text).

At room temperature $Pt(thpy)_2$ shows a luminescence band with maximum at 580 nm, with lifetime in the microsecond range, assigned as a MLCT phosphorescence.[8] The phosphorescence intensity and lifetime were found to increase by a factor of 15 upon deaeration of the solution. The first-order rate constant of phosphorescence decay was 3.3×10^{-5} s^{-1} (τ = 3.0 μs) in degassed CH_2Cl_2 solution at room temperature. The presence of anthracene did not modify the emission spectrum but quenched the phosphorescence intensity with a bimolecular quenching constant ($1.0 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}. The phosphorescence lifetime was quenched in parallel with the phosphorescence intensity. The Stern–Volmer quenching plots are reported in Figure 5.

The photochemical behavior of $Pt(thpy)_2$ was qualitatively the same in the absence or in the presence of anthracene, but the photochemical quantum yield was found to decrease with increasing anthracene concentration up to a limiting value, as shown in Figure 5.

For CH_3CN/CH_2Cl_2 mixtures, emission intensity and lifetime were almost unaffected (or, at most, increased slightly) as the CH_2Cl_2 concentration increased (Table I).

Discussion

Solvent Effects. The absorption spectrum of $Pt(thpy)_2$ (Figure 1) shows a relatively intense and composite band in the visible, which is assigned to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions and some more intense bands in the UV region assigned to ligand-centered transitions.[8] From CH_3CN to CH_2Cl_2 or $CHCl_3$, there are slight but clearly appreciable spectral changes. In particular, several bands appear in the difference spectra. Most likely, these differences are mainly due to solvent shifts of the "intramolecular" electronic transitions involving orbitals of different localization. Some contribution from charge transfer to solvent (CTTS) bands[27–29] is also plausible since the complex is relatively easy to oxidize[30] and the halogenated solvents are relatively easy to reduce.[31]

As one can see from Table I, the complex is practically photoinert in deaerated CH_3CN solutions and photoreactive in CH_2Cl_2 and $CHCl_3$ or in CH_3CN solutions that contain a sufficiently large amount of CH_2Cl_2. In the CH_3CN/CH_2Cl_2 mixed solvents, the

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quantum yield of the photoreaction increases with increasing CH_2Cl_2 concentration, but this increase is not accompanied by a corresponding decrease in luminescence intensity or lifetime of the MLCT excited state. This suggests that the ^{3}MLCT excited state is not heavily involved in the photochemical reaction.

In deaerated $CHCl_3$ solution, the quantum yield for 313-nm excitation is larger than unity and postphotochemical effects were observed. This shows that, at least under such experimental conditions, the photoreaction proceeds essentially via a chain mechanism as previously found for other photooxidative addition reactions.[21,28,32-34]

Wavelength Effect. In deaerated CH_2Cl_2 solution, the quantum yield of the luminescence emission is practically unaffected by the excitation wavelength, as shown by the proportionality between the absorption and excitation spectra (within 10% experimental uncertainty). This implies that, regardless of whether excitation is carried out in the ligand-centered or MLCT bands, there is essentially the same efficiency of conversion to the luminescent ^{3}MLCT excited state. This is likely to happen only if such an efficiency is practically unity in both cases. By contrast, the quantum yield of the photoreaction is strongly wavelength dependent (Table I). The decrease of the photoreaction quantum yield on going from 313- to 430-nm excitation rules out any simple mechanism based on a thermally equilibrated, reactive excited state.

Quenching by Anthracene. The results obtained show that the luminescent ^{3}MLCT excited state of $Pt(thpy)_2$ is dynamically quenched by anthracene (Figure 5) at a rate close to diffusion controlled. As discussed in more detail elsewhere,[35] the dynamic quenching of an excited state in fluid solution can take place by several distinct mechanisms, but diffusion (or close to diffusion) controlled quenching constants can only be obtained when energy or electron-transfer processes are operative. The oxidation and reduction potentials (vs SCE) are >−1.35 and +0.36 V for $(^3MLCT)Pt(thpy)_2$[36] and +1.09 and −1.92 V for anthracene.[31] This means that both oxidative and reductive electron-transfer quenching processes are thermodynamically forbidden. By contrast, energy transfer from $(^3MLCT)Pt(thpy)_2$ ($E^{\infty} = 2.17$ eV)[8] to ground-state anthracene to yield the lowest triplet excited state of anthracene ($E^{\infty} = 1.82$ eV)[38] is allowed and must thus be the process responsible for the observed quenching. Incidentally, such an energy-transfer mechanism guarantees that the quenching of $(^3MLCT)Pt(thpy)_2$ by anthracene does not "dirty" the photochemical reaction of $Pt(thpy)_2$ under quenching conditions.

A very interesting result is the following. Whereas the quenching of the $(^3MLCT)Pt(thpy)_2$ luminescence intensity or lifetime gives rise to a regular Stern–Volmer linear plot, the plot for the quenching of the $Pt(thpy)_2$ photoreaction is not linear and reaches a plateau value for large quencher concentrations (Figure 5). This shows that only part of the photochemical reaction can be quenched on complete quenching of the ^{3}MLCT excited state of the complex. As better shown by the Φ_r/Φ_r^0 vs I/I^0 or τ/τ^0 plot (Figure 5, inset), where Φ_r, Φ_r^0, I, I^0, τ, and τ^0 are the photoreaction quantum yields, the emission intensities, and the emission lifetimes, respectively, in the presence and in the absence of the quencher, the unquenchable part of the photoreaction amounts to ~25% for 430-nm excitation. For 313-nm excitation, the unquenchable part of the photoreaction is noticeably larger (~60%). It should also be noted that partial light absorption by anthracene, as it happens for the 313-nm excitation experiments, is not expected to cause any trouble because anthracene is not photosensitive in CH_2Cl_2 and its singlet excited state is too short lived (5 ns)[38] to give rise to bimolecular processes with $Pt(thpy)_2$.

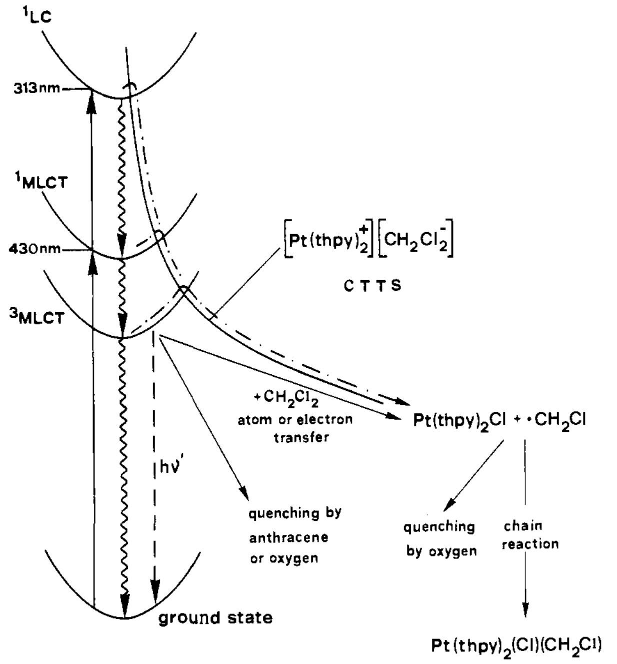

Figure 6. Pictorial representation of the excited-state mechanism of the photoreaction of $Pt(thpy)_2$ with CH_2Cl_2.

Thus, the results concerning quenching by anthracene clearly indicate that at least part of the photoreaction takes place from excited state(s) different from the luminescent ^{3}MLCT excited state. Subdivision of the overall photoreaction quantum yields into quenchable (Φ_r^q) and unquenchable (Φ_r^u) parts gives the following values: λ_{exc} (313 nm), $\Phi_r^q = 0.1$ and $\Phi_r^u = 0.2$; λ_{exc} (430 nm), $\Phi_r^q = 0.08$ and $\Phi_r^u = 0.02$. One can see that the higher value of the overall quantum yield upon 313-nm excitation is essentially due to a higher unquenchable contribution while the quenchable quantum yields are essentially the same (within experimental error) at the two wavelengths.

Quenching by Oxygen. The results obtained in aerated and deaerated solutions show that there is a quenching effect by oxygen on both the luminescence emission and the photochemical reaction. The quenching effect on the initial quantum yield of the photochemical reaction is clearly much larger than the quenching effect on the luminescence lifetime, in contrast with the results obtained when the quencher is anthracene. For example, for CH_2Cl_2 solutions a quenching of the luminescence lifetime by a factor of 15 corresponded to a quenching of the photoreaction quantum yield ($\lambda_{exc} = 313$ nm) by a factor 1.5 for anthracene and 60 for oxygen. This suggests that oxygen exhibits a quenching action not only on the luminescent ^{3}MLCT state but also on other species (presumably radicals, see later text) involved in the photoreaction. Furthermore, the oxygen-quenching effect on the photoreaction is larger for $CHCl_3$ than for CH_2Cl_2 solutions (Table I). The increase in the quantum yield of the photoreaction with increasing irradiation time for aerated solutions (Figure 3b) suggests that oxygen is consumed as a consequence of the photoreaction.

Photoreaction Mechanism. The results discussed above allow us to draw the following conclusions:

(i) Regardless of the irradiation wavelength, a fraction close to unity of the excited states obtained upon light absorption undergoes deactivation to the lowest excited state, which is the luminescent ^{3}MLCT state.

(ii) The photoreaction proceeds largely via species unquenchable by anthracene (which quenches the lowest excited state, ^{3}MLCT) but quenchable by oxygen. Such species have to be radicals since any upper excited state of the complex is expected to have a lifetime too short to be quenched by small oxygen concentrations as such found in aerated solvents.

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(iii) The involvement of radicals is confirmed by the chain nature of the photoreaction shown by the higher than unity quantum yield obtained in degassed $CHCl_3$ solution.

(iv) The radicals responsible for the part of the photoreaction that is unquenchable by anthracene are generated in higher concentrations upon 313-nm excitation.

(v) The ^{3}MLCT state is the reactive excited state or a precursor of the reactive excited state responsible for that part of photoreaction quenchable by anthracene.

The observed photochemical behavior may be explained on the basis of the excited-state mechanism pictorially shown in Figure 6. Light excitation at 313 or 430 nm is followed by an almost complete internal deactivation to the luminescent ^{3}MLCT excited state. However, small fractions of the ^{1}LC (ligand-centered) and ^{1}MLCT excited states are converted to a charge transfer to solvent state, which undergoes dissociation into a pentacoordinated Pt(III) intermediate and a CH_2Cl radical.[39] The fraction of photoreaction that proceeds through this way cannot be quenched on quenching ^{3}MLCT by anthracene. The quenchable (by anthracene) part of the photoreaction may originate either by population of the CTTS excited state via the thermally equilibrated ^{3}MLCT or by an atom- or electron-transfer reaction taking place between ^{3}MLCT and CH_2Cl_2. It should be noticed that, because of the chain nature of the process (vide infra), only a very small fraction of ^{3}MLCT excited states needs to be involved in these reactive processes. Therefore, no quenching effect of CH_2Cl_2 on ^{3}MLCT needs to be seen.

The mechanism of the secondary radical chain reactions (and of their quenching by oxygen) that lead to the formation of the final products is presumably similar to that discussed by other authors in dealing with oxidative addition reactions.[16,21,32,33,40,41] The primary photochemical processes described in the scheme of Figure 6 can be summarized by eq 1. The pentacoordinated

$$\mathrm{Pt(thpy)_2 + CH_2Cl_2 \xrightarrow{h\nu} Pt(thpy)_2Cl + {}^{\bullet}CH_2Cl} \qquad (1)$$

Pt(III) complex so obtained may undergo a (cage) recombination with the $^{\bullet}CH_2Cl$ radical to give the final Pt(IV) product (eq 2)

$$\mathrm{Pt(thpy)_2Cl + {}^{\bullet}CH_2Cl \rightarrow Pt(thpy)_2(Cl)(CH_2Cl)} \qquad (2)$$

or a Cl abstraction from CH_2Cl_2 to yield a dichloro Pt(IV) complex and a $^{\bullet}CH_2Cl$ radical (eq 3). The $^{\bullet}CH_2Cl$ radicals

$$\mathrm{Pt(thpy)_2Cl + CH_2Cl_2 \rightarrow Pt(thpy)_2Cl_2 + {}^{\bullet}CH_2Cl} \qquad (3)$$

produced in the primary photoreaction 1 or in reaction 3 may react with $Pt(thpy)_2$ to give either a pentacoordinated Pt(III) complex (eq 4) or nonradical products presumably via addition to the ligands (eq 5). Alternatively, they may undergo bimolecular

$$\mathrm{{}^{\bullet}CH_2Cl + Pt(thpy)_2 \rightarrow Pt(thpy)_2CH_2Cl} \qquad (4)$$

$$\mathrm{{}^{\bullet}CH_2Cl + Pt(thpy)_2 \rightarrow nonradical\ products} \qquad (5)$$

recombination (eq 6). Finally, the Pt(III) complex generated

$$\mathrm{{}^{\bullet}CH_2Cl + {}^{\bullet}CH_2Cl \rightarrow C_2H_4Cl_2} \qquad (6)$$

by reaction 4 may give Cl abstraction from CH_2Cl_2 to yield the final Pt(IV) complex and regenerate a $^{\bullet}CH_2Cl$ radical (eq 7). Reactions 2 and 6 are expected to be negligible because they are second order in radical species.

$$\mathrm{Pt(thpy)_2CH_2Cl + CH_2Cl_2 \rightarrow Pt(thpy)_2(Cl)(CH_2Cl) + {}^{\bullet}CH_2Cl} \qquad (7)$$

In the presence of oxygen, the $^{\bullet}CH_2Cl$, $Pt(thpy)_2Cl$, and $Pt(thpy)_2CH_2Cl$ radicals can be scavenged. For concentration reasons, however, the $Pt(thpy)_2Cl$ and $Pt(thpy)_2CH_2Cl$ species will continue to react with the CH_2Cl_2 solvent (eq 3 and 7) and the photochemical behavior is affected mainly because of the reduction in the concentration of the $^{\bullet}CH_2Cl$ chain carrier. As we have seen before under conditions of equal emission quenching, the reaction quenching by oxygen is about 40 times higher than that caused by anthracene.[42,43] This suggests that each $^{\bullet}CH_2Cl$ radical generated in reactions 1 and 3 carries a chain of ~40 steps. This is consistent with a negligible concentration of Pt products different from $Pt(thpy)_2(Cl)(CH_2Cl)$. This mechanism is also consistent with the observed independence of the quantum yield on complex concentration (and thus, on absorbed light intensity) (Figure 3a), which requires[21] that the termination step involve the $Pt(thpy)_2$ complex (eq 5).

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Registry No. Anthracene, 120-12-7; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; O_2, 7782-44-7; $Pt(thpy)_2$, 100012-12-2; $Pt(thpy)_2(Cl)(CH_2Cl)$, 103933-71-7; $Pt(thpy)_2(Cl)(CHCl_2)$, 103933-72-8; $Pt(thpy)_2Cl$, 110904-97-7; $Pt(thpy)_2Cl_2$, 110904-98-8.

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[39] An alternative but equivalent mechanism would be a static electron-transfer quenching of ^{1}LC and ^{1}MLCT by solvent CH_2Cl_2 molecules.

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[41] Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80.

[42] This figure has been obtained in air-saturated solution. Larger oxygen concentration would certainly have a larger effect.

[43] Under oxygen-quenching conditions, one can expect that a larger amount of the side product $Pt(thpy)_2Cl_2$ should be formed. This can account for the small spectral differences observed for aerated and deaerated solutions (see Results).