

PHOTOPHYSICAL INVESTIGATION OF
IRIDIUM-CARBON SIGMA BONDED COMPLEXES

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SANTA BARBARA

**STRUCTURAL CHARACTERIZATION AND
PHOTOPHYSICAL INVESTIGATION OF
IRIDIUM-CARBON SIGMA BONDED COMPLEXES**

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in

Chemistry

by

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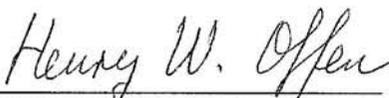
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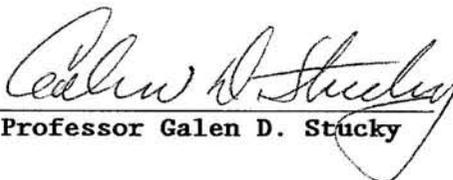
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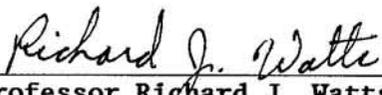
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I would like to dedicate my dissertation
to the ones I love most,
my family.

To mom and dad (Nieves and Joe),
thank you for the support—
spiritual, emotional and financial.
thank you for never letting me doubt myself
and my abilities.
most of all thank you for being my parents.
To Noel, Lelian and Grace,
thank you for always being patience with me
and challenging me always to do better.
And especially to Will,
thank you for always putting our needs
in front of your own.
your example of hard work and determination has
always been an inspiration to me.

Most of all, thank you all for always being there for me.

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"Synthesis and Photophysical Studies of Ortho-Metalted Pd(II) Complexes Including Two Novel Pd(II)/Rh(III) Dimers"; C.A. Craig, F.O. Garces, R.J. Watts; *Ibid.*,

"Synthesis, Structure, ElectroChemistry and Photophysics of Methyl-Substituted Phenylpyridine Ortho-metalted Ir(III) Complexes"; Fred O. Garces, K.A. King, R.J. Watts, Inorganic Chemistry 1988, 27 3464.

"A New Ortho-Metalted Dichloro-Bridged Complex of Ir(III) with 2,2'-bipyridine: $[\text{Ir}(\text{bpy-C}^3, \text{N}')(\text{bpy-N, N}')\text{Cl}]_2\text{Cl}_2$ "; Fred O. Garces, Richard J. Watts, Inorganic Chemistry, In Press.

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7/88 "[Ir(bpy-C³,N')(bpy-N,N')Cl]₂Cl₂, the first dichloro-bridged dimer of a bipyridine complex of Ir(III)"; Southern California Inorganic Photochemical Conference, Lake Cachuma, University of California, Santa Barbara, California.

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"Photophysical Investigation of Palladium (II) Ortho-Metalates"; Carl A. Craig, Fred O. Garces, Richard J. Watts, Pacific Conference on Chemistry and Spectroscopy, Irvine, CA., October 28-30, 1987.

"Excited State Characterization of Chemically-Modified Ortho-metalating complexes"; F.O. Garces, M. Libunao, M. Torres, S. Tellechea, and R.J. Watts, SACNAS Conference, El-Paso, Texas, October 29-31, 1987.

"Analysis of the ^1H and ^{13}C NMR spectra of $[\text{Ir}(\text{bpy}-\text{C}^3, \text{N}')(\text{bpy}-\text{N}, \text{N}')\text{Cl}]_2^{2+}$: Evidence for a Carbon Bonded Structure"; Fred O. Garces, P.J. Spellane, R.J. Watts, NMR Dedication Ceremony, Santa Barbara, CA., January 7, 1987.

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"Photophysical Properties of Ortho-metalated Complexes of Palladium (II)"; C.A.Craig, F.O.Garces, R. J. Watts, Southwestern Regional ACS conference, Las Vegas, Nv., March 9, 1987.

"Ground and Excited State Properties of Cyclo-Metalated Iridium (III) Complexes: A Potential Photocatalyst"; Fred O. Garces, R.J. Watts, Southwestern Regional ACS conference, Las Vegas, Nv., March 9, 1987.

"Structural and Photophysical Studies of Metal-Carbon Sigma-Bonded Species: New Ortho-Metalated Complexes of 2,2'-Bipyridine, R.J. Watts, F.O. Garces, A.P. Wilde, C. Miller, Twelfth DOE Solar Photochemistry Research Conference, Washington D.C., May 23, 1988.

" ^1H and ^{13}C NMR Analysis of $[\text{Ir}(\text{bpy}-\text{C}^3, \text{N}')(\text{bpy}-\text{N}, \text{N}')\text{Cl}]_2$: Evidence for an Ortho-Metalated Dimer Structure"; Fred O. Garces, P.J. Spellane, R.J. Watts, 195th ACS National Conference, Toronto, Canada, June 5-10, 1988.

"Photophysics of Ortho-metalated Palladium(II) and Rhodium(III) Complexes, C.A. Craig, F.O. Garces, R.J. Watts, 195th ACS National Conference, Toronto, Canada, June 5-10, 1988.

"Temperature and Solvent Dependence of Absorption and Emission of Ortho-metalated Complexes of Ir(III)"; A.P. Wilde, K. A. King, C. Miller, F. O. Garces, R. J. Watts, XII IUPAC Symposium on Photochemistry, Bologna, Italy, July 17, 22, 1988.

"Structural and Photophysical Investigation of $[\text{Ir}(\text{bpy}-\text{N}, \text{N}')(\text{bpy}-\text{C}^3, \text{N}')\text{Cl}]_2^{2+}$: A Dichloro-bridged Ortho-metalated Dimer"; F.O. Garces, P.J. Spellane, R.J. Watts, XII IUPAC Symposium on Photochemistry, Bologna, Italy, July 17, 22, 1988.

INTRAMURAL GRANTS

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ABSTRACT

STRUCTURAL CHARACTERIZATION AND PHOTOPHYSICAL INVESTIGATION OF IRIDIUM-CARBON SIGMA BONDED COMPLEXES

by

Fred Omega Garces

The purpose of the work in Part I was to explore the enhancement of the already-high photoreducing potential of ortho-metalated complexes such as $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ and $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$ by introducing functional groups onto the ppy ligand. The ligands 3-methyl-2-phenylpyridine (mppy) and 2(p-tolyl)pyridine (ptpy), which contain methyl groups donating electron density to either the phenyl ring (ptpy) or the pyridyl ring (mppy) were used for this purpose. In the course of this investigation, structural characterizations by NMR techniques and crystallographic analysis indicated that these complexes possess mutually cis Ir-C bonds; the dimers are D_2 symmetric and the monomers are C_2 symmetric. ^1H and ^{13}C resonances were completely assigned in the NMR spectra.

Electrochemical and photophysical investigations suggest that the electron density about the iridium metal of these complexes are enhanced by the modification of ppy ligands. Our results show that

these methyl-substituted ortho-metalated iridium complexes are much stronger photoreducing agents than their non-substituted counterparts.

Preparation and characterization of four novel iridium bipyridyl complexes are discussed in Part 2 of this dissertation. Iridium (IV) seems to be a key ingredient in the preparation of these complexes. Structural characterizations suggest that the first of these bpy complexes is an ortho-metalated dichloro-bridged bpy dimer, $[\text{Ir}(\text{bpy-C}^3, \text{N}')(\text{bpy-N, N}')\text{Cl}]_2^{2+}$, I. Characterizations of I include, ^1H and ^{13}C NMR spectroscopic; mass spectroscopic; electrochemical; photophysical (including acid / base measurements) techniques.

The second complex exists as a $[\text{Ir}(\text{Hbpy-C}^3, \text{N}')(\text{bpy-N, N}')\text{Cl}_2]^+$ cation and an $[\text{IrCl}_4(\text{bpy})]^-$ anion in an ion pair arrangement as shown by crystallographic techniques, II. NMR and mass spectroscopy provide good evidence for ortho-metalated bpy ligands in the cationic moiety.

Our spectroscopic and elemental analysis evidence for the third complex suggest an Ir(IV), cis- $[\text{Ir}^{\text{IV}}(\text{bpy-N, N}')_2\text{Cl}_2]^{+2}$ species, III. And finally the fourth complex isolated has been identified as the trans- $[\text{Ir}(\text{bpy})_2\text{Cl}_2]^+$, IV.

The last chapter describes other ortho-metalated iridium (III) complexes similar to those described in Part I. NMR spectroscopic and photophysical results are presented.

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FORWARD

This dissertation covers two major area of research. The first is ortho-metalated iridium 2-phenylpyridine complexes in which the ppy ligand has been structurally modified by a methyl group either in the phenyl ring (ptpy) or pyridyl ring (mppy). Structural and photophysical characterization of these complexes is described in Part I, Chapters 2, 3 and 4.

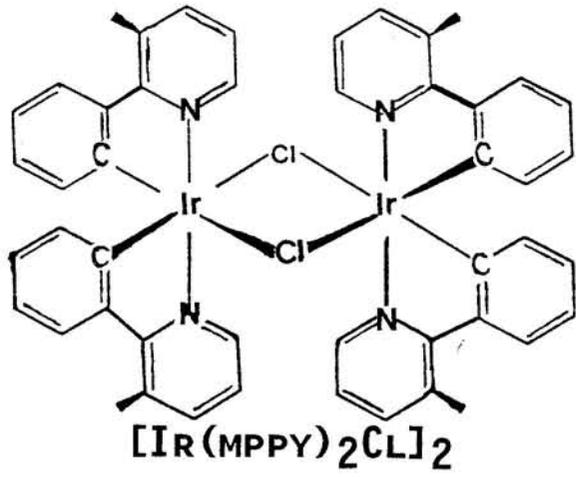
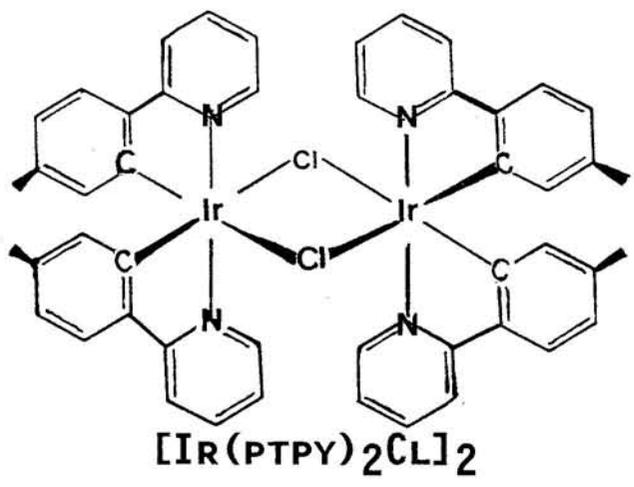
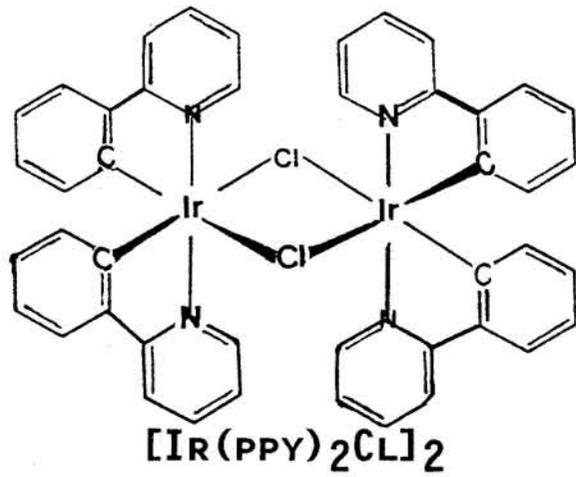
The second major area of research is one I have been involved with for just this past year. It involves iridium bipyridyl complexes. Using Ir(IV) in the synthetic procedure results in four novel complexes. Our results show that two of these are ortho-metalated bpy complexes. The emphasis in Part 2, Chapters 5 and 6, is the structural characterization of these four bpy complexes.

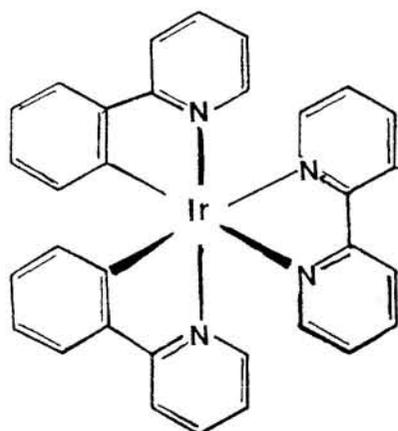
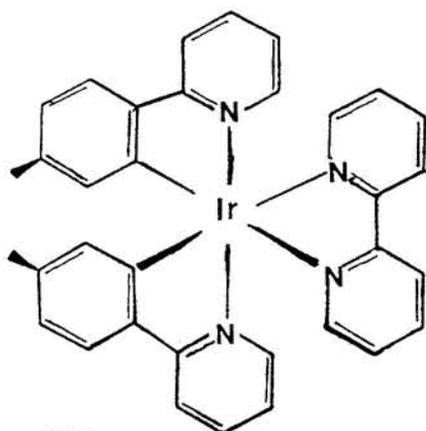
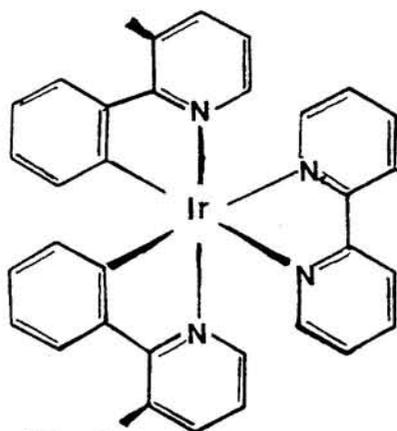
A general overview of photochemistry is described in Chapter 1. This chapter is intended to give a simplified view of how the measurements in the thesis relates to photoconversion system.

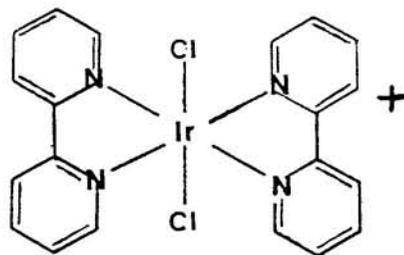
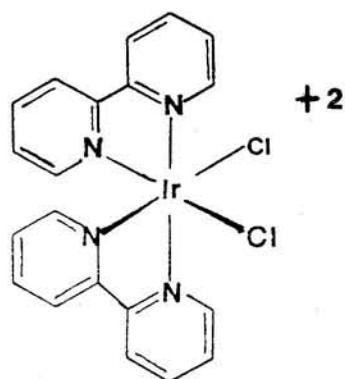
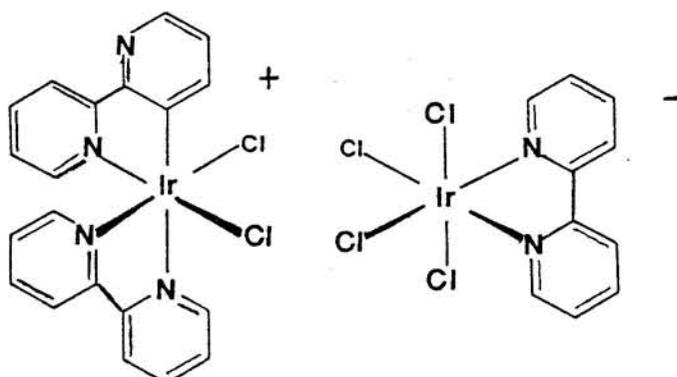
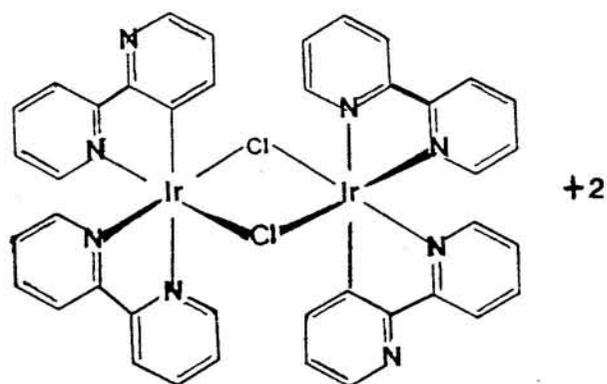
Chapter 7 presents some ortho-metalated iridium complexes which I prepared or characterized during my tenure here.

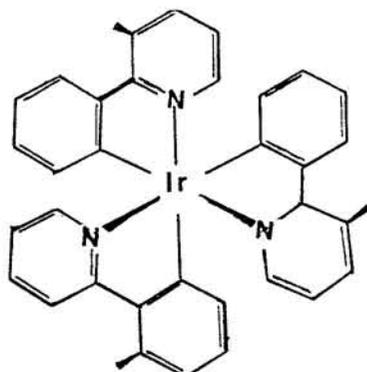
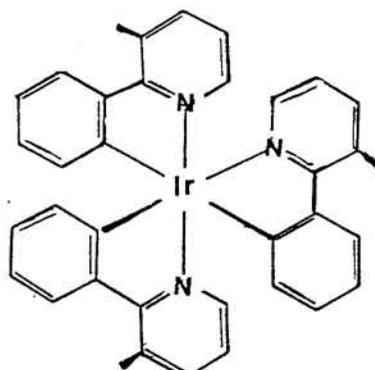
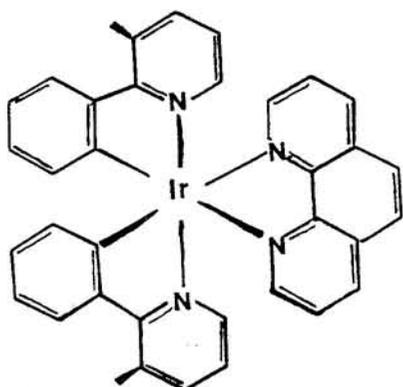
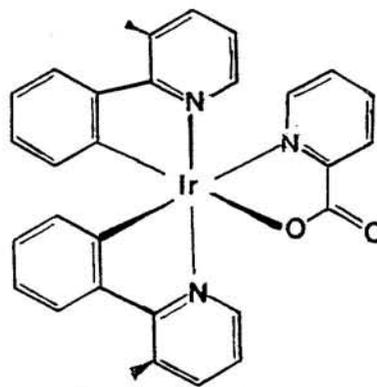
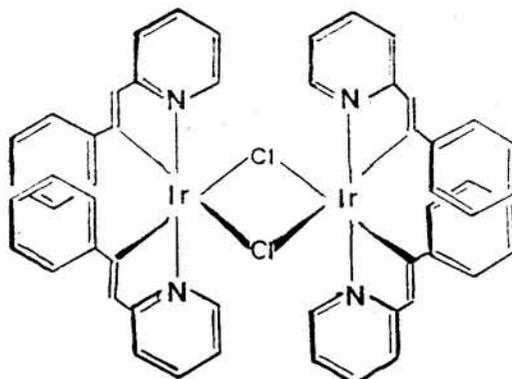
The appendix is a package of experimental procedures. NMR is discussed in great length because of its significant in my research. Also in the appendix is an extension of the acknowledgement page found in page iii.

The following are structural representations of all the iridium complexes discussed in this dissertation.



 $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$  $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$  $[\text{Ir}(\text{mppy})_2\text{bpy}]^+$



**FAC-Ir(MPPY)₃****MER-Ir(MPPY)₃****[Ir(MPPY)₂PHEN]⁺****Ir(MPPY)₂PIC****[Ir(STPY)₂Cl]₂**

CHAPTER 1

**ORTHO-METALATED COMPLEXES AND STORAGE OF SOLAR ENERGY:
A GENERAL OVERVIEW.**

*The whole of science is nothing more
than a refinement of everyday thinking.*

- Albert Einstein

Our group started research in ortho-metalated complexes when Professor Watts first discovered an isomer of $\text{Ir}(\text{bpy})_3^{3+}$.^{1,2} The structure of this isomer, $[\text{Ir}(\text{bpy}-\text{C}^3, \text{N})(\text{bpy}-\text{N}, \text{N}')_2]^{2+}$, was the center of numerous debates, which were finally settled by crystallographic analysis.^{3,4} The crystal structure showed that the product in question possesses two normal chelating bpy ligands while the third was bound to the iridium center via metalation; through the N' atom from one pyridyl ring and the C³ atom of the other pyridyl ring, Figure 1.1. Later Watts et al. showed that the structure of this isomer in solution is similar to that in the solid state.⁵ NMR analysis included two dimensional shift correlation spectroscopy (COSY) to assist in the assignment of all the proton resonances in the ¹H NMR spectrum and to provide insight on the electronic

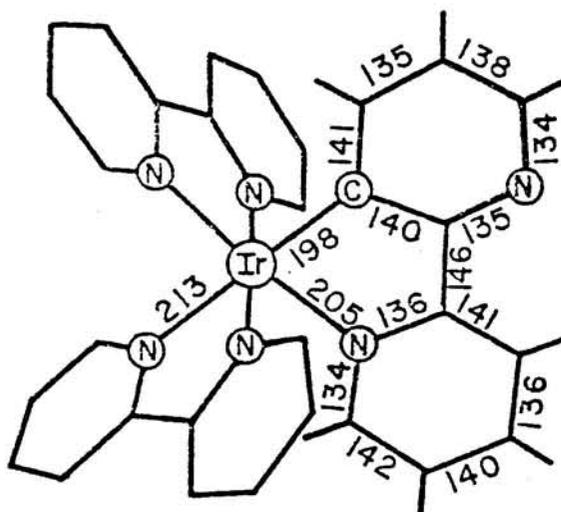


FIGURE 1.1

Structure of $[\text{Ir}(\text{bpy-C}^3, \text{N})(\text{bpy-N, N}')_2]^{2+}$.³

properties of the complex. It was this pioneering work with $[\text{Ir}(\text{bpy-C}^3, \text{N}')(\text{bpy-N, N}')_2]^{2+}$ which led our research group to the study of ortho-metalated complexes and to rely on NMR techniques for the elucidation of molecular structures.

The topics of research presented in this dissertation involve the structural characterization and photophysical investigation of iridium-carbon σ -bonded complexes which are capable of photosensitizing chemical reactions for solar storage via fuel generation. The experimental arsenal covers (1) synthetic schemes to prepare targeted complexes, (2) NMR techniques and X-ray crystallography to elucidate structures, (3) cyclic voltammetry to determine potentials of the ground state, (4) absorption, emission and excited state absorption measurements to characterize the excited state, (5) laser spectroscopy, Stern-Volmer quenching and

quantum yield measurements to monitor lifetimes and understand electron and energy transfer processes. Furthermore, investigation on the dependence of temperature, solvent, excitation and pH were used to elucidate electronic transitions in some of these complexes. Ultimately, results from these experiments will enable us to determine the viability of these complexes as photoreagents.

The development of solar-driven artificial processes (photoconversion systems) that convert abundant resources into chemical fuels, e.g., $2\text{H}_2\text{O} + h\nu \longrightarrow 2\text{H}_2 + \text{O}_2$ is important if only to sustain current energy requirements for the near future. Photoconversion mechanisms in photobiology, photoelectrochemistry, photovoltaics and photochemistry provide systems capable of harnessing the sun's energy cleanly and efficiently.⁶ More recently, Jean-Marie Lehn suggests the development of supramolecular devices for this purpose.⁷ The main component fundamental to the photoconversion system is the photosensitizer. Characterization of complexes capable of photosensitizing chemical reactions is the focus of research in Professor Watts' laboratory.

Kutal⁸ describes the main components of a photoconversion system, Figure 1.2, in which solar irradiation drives a photochemical reaction in a thermodynamically unfavorable direction, $\Delta G > 0$, to form products (chemical fuel). Photosensitizers are used to absorb the incident light because in most instances the reactant(s) do not absorb solar irradiation. Reversal of the cycle by application of heat or catalyst, liberates the stored energy.

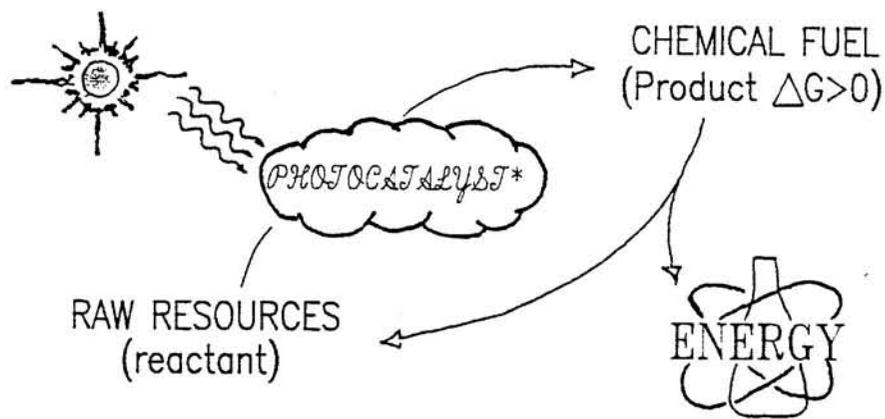


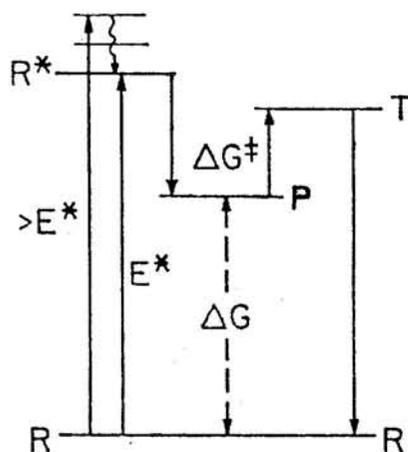
FIGURE 1.2

Fundamental components of an abiotic photoconversion system.⁸

This system will most likely require electron relays and redox catalysts in addition to the ones already mentioned. Nevertheless, as mentioned, the gist of a photoconversion system is the photosensitizer and its ability to absorb electromagnetic radiation, preferably at wavelengths utilizing the solar spectral range and then, through its excited state, activate inert substrates such as H_2O and CO_2 in order to transform optical energy to chemical potential energy stored in bonds. The photo-generation of excited state precursors (substrate bound to the metal catalyst) having sufficient redox potentials leads to substrate reduction or oxidation via multi-electron transfer processes which are necessary for product formation.

Kutal,⁸ Bolton⁹ and Balzani¹⁰ discuss several criteria fundamental for a viable photoconversion energy storage cycle. These criteria are: (1) The reactions in the photochemical cycles should be capable of operating over a wide band width of the visible and ultraviolet portion of the solar spectrum with a threshold wavelength well into the red or near infrared. In other words, the photosensitizer should absorb visible light. (2) The photochemical reaction must be endergonic, $\Delta G > 0$. That is, upon absorption of electromagnetic radiation the system must proceed in the thermodynamically unfavorable direction. (3) The endergonic photoreactions must be cyclic with only raw materials and solar irradiation being consumed. That is, the photosensitizer must be regenerated after each cycle. (4) The quantum yield should be near unity. The efficiency of converting absorbed photons to chemical energy must be high. (5) For long term storage of the products, the back reaction must be extremely slow under ambient conditions. Furthermore, upon heating or addition of catalyst, the back reaction should proceed controllably, rapidly and specifically. (6) To ensure maximum efficiency, side reactions leading toward the depletion of photosensitizers, reactants, products and/or catalysts must be at a minimum. (7) Finally, reagents and other necessary components of the photoconversion system should be available, manageable, inexpensive and nontoxic.

There are inherent limitations in photoconversion processes aside these stringent requirements which limit the overall



ENERGY STORAGE: $R \xrightarrow{h\nu} P$

ENERGY RELEASE: $P \xrightarrow[\text{catalyst}]{\text{heat}} R$

FIGURE 1.3

Energy diagram for photoconversion storage cycle.⁸

efficiency of converting solar energy to chemical fuel.^{8,11} Figure 1.3 illustrates an energy diagram for a photoconversion process. The diagram shows that only photons with energies corresponding to E^* will be absorbed by the reactant R, without significant waste. Photons having energies less than the threshold value E^* , will not be absorbed. Furthermore, absorption of photons having energies greater than E^* results in the population of vibrationally excited levels of R^* ; internal conversion results in the lowest vibrational level of R^* to be populated and any energy in excess of E^* is lost to the surroundings. In addition to absorption losses, the conversion of raw materials to useful fuels will require free energy from the system to prevent the back reaction. As such, the available energy corresponds to ΔG and not E^* ; the system will in effect lose energy due to storage.

Ross and Hsiao et al.¹², calculated the maximum thermodynamic efficiency for an abiotic solar conversion system to be 32% at 840 nm, taking into consideration the fraction of solar power available at the bandgap energy. If losses due to an activation barrier (ΔG^\ddagger) are figured into the calculation, the gross efficiency drops to $9.2 \pm 0.8\%$. This, however, is still comparable to the $5.6 \pm 1.2\%$ efficiency for photosynthesis.¹³

TABLE 1.1

Endergonic fuel-generation reactions

Reaction	ΔG (KJ/mol)	n (mol)	E (V)
$\text{H}_2\text{O}(l) + h\nu \longrightarrow \text{H}_2(g) + 1/2 \text{O}_2(g):$	237	2	1.23
$\text{CO}_2(g) + 2\text{H}_2\text{O}(l) + h\nu \longrightarrow$ $\text{CH}_3\text{OH}(l) + 3/2 \text{O}_2(g):$	703	6	1.21
$\text{CO}_2(g) + 2\text{H}_2\text{O}(l) + h\nu \longrightarrow$ $\text{CH}_4(g) + 2\text{O}_2(g):$	818	8	1.06
$\text{N}_2(g) + 3\text{H}_2\text{O}(l) + h\nu \longrightarrow$ $2\text{NH}_3(g) + 3/2 \text{O}_2(g):$	678	6	1.17

Raw materials for photoconversion processes are readily available from our environment. Economical, ecological and energetic considerations indicate that water, carbon dioxide and dinitrogen are the most attractive raw materials for photoconversion

processes. Table 1.1 shows some of the thermodynamic parameters of some endergonic fuel generation reactions⁹.

All the reactions shown in Table 1.1 involve multi-electron changes. Herein lies the problem; photoredox reactions of transition metal complexes generally occur with the transfer of only one electron per absorbed photon. How can a one-electron redox process satisfy a multi-electron reaction in such a way as to avoid formation of high energy radicals that retard the efficiency of the photoconversion process? The answer lies in charge-storage catalyst whose role is to mediate multi-electron changes by accumulating the proper number of electrons for delivery to the reactants and furthermore stabilizing any intermediates that form.

Traditional photosensitizers charge-storage catalyst such as $\text{Ru}(\text{bpy})_3^{2+}$ operate in aqueous media. However, recent emphasis has been toward the development of complexes capable of operating in both aqueous and nonaqueous media and possessing multiple functionality as photosensitizer / relay / catalyst. Functions of metal complexes may be classified as: (1) electron relays in order act as intermediate electron storage devices, (2) redox catalysts to enhance the rate of the redox processes, and (3) redox substrates to regenerate the photosensitizer or catalyst. The ability of a metal complex to play multiple roles in photoconversion systems is contingent on its excited state (as well as ground state) properties.

The excited states of metal complexes are useful in photochemical conversion because they participate in rapid outer sphere electron transfer, sustain long lifetimes, possess favorable redox potentials and are accessible by absorption of visible light. Balzani¹⁰ points out that an excited state induced in a molecule by absorption of light becomes virtually a new species with its own chemical and physical properties distinct from those corresponding to the ground state molecule. In the excited state, the molecule has a higher electron affinity and a lower ionization potential. This asset makes the excited state a better oxidant and a better reductant than that of the ground state.

The Latimer diagram of $\text{Ru}(\text{bpy})_3^{2+}$, Figure 1.4, shows that the excited state is both a moderately strong oxidant (-0.86 V vs. NHE) and a very strong reductant ($+0.84 \text{ V}$) compared to the ground state

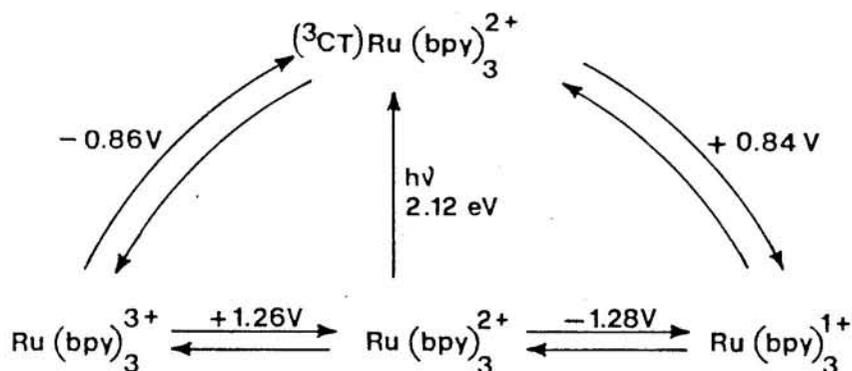


FIGURE 1.4

Latimer diagram for $\text{Ru}(\text{bpy})_3^{2+}$ (vs. NHE).¹⁰

which has an oxidation and reduction potential of +1.26 and -1.28 V, respectively. Moreover, the excited state redox potential of metal complexes such as $\text{Ru}(\text{bpy})_3^{2+}$, may be altered ("tuned") by several types of structural modifications. Modifications include: (1) changing the central metal, (2) replacing some or all of the ligands with other suitable ligands i.e., 2-phenylpyridine (ppy), (3) modifying the ligands by adding suitable functional groups, and (4) using mixed bimetallic complexes to access, within a single chemical moiety, redox properties associated with each monomeric complex.

Changing the metal in $\text{Ru}(\text{bpy})_3^{2+}$ to Ir(III) for example, produces a complex, $\text{Ir}(\text{bpy})_3^{3+}$, with excellent photo-oxidizing power (~2 V vs. NHE).¹⁴ On the other hand, replacing bpy in $\text{Ir}(\text{bpy})_3^{3+}$ with ppy produces a very strong photo-reductant, $\text{Ir}(\text{ppy})_3$.¹⁵ Species containing both bpy and ppy coordinated to a common metal ion center such as in $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$, have intermediate photoredox capabilities and can operate as either photo-oxidants or photo-reductants.¹⁶ Thus, the optimization of photoredox properties of metal complexes can be provided by the combination of ortho-metalating ligands such as ppy and its derivatives with coordinating ligands such as bpy.

The metal-carbon bond in ortho-metalated complexes can be described as a 2-electron, 2-center covalent σ -bond with bonding density along the metal-carbon internuclear axis. The intriguing properties manifested from the metal carbon σ -bond make ortho-metalated complexes viable for many photosensitizer applications.

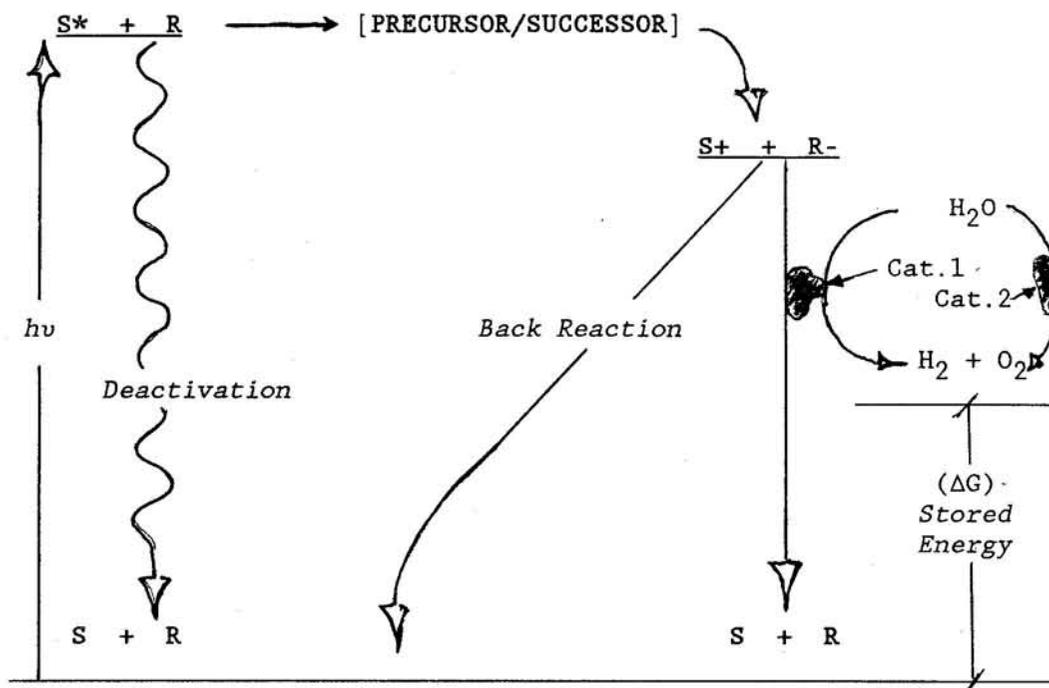


FIGURE 1.5

Energy reaction coordinate diagram for substrate (S) and reactant (R) undergoing electron transfer processes.¹⁹

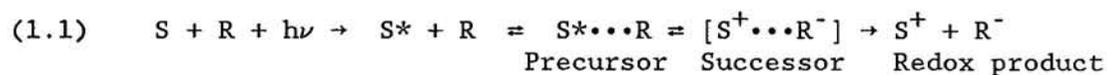
Favorable properties imparted through ortho-metalation include:^{17,18}

- 1) An enhancement of the excited state redox potential to drive endergonic chemical reactions as a consequence of the increase of the energy of metal-localized states because of the greater ligand field strength of ppy over bpy.
- 2) The availability of low-lying MLCT states from the enhancement of electron density about the metal center from the strong σ -donor ability of the metal-carbon bond.
- 3) Cathodic shift in the oxidation potential of the metal center in

ortho-metalated complexes giving rise to very strong photoreductants but relatively weak photooxidants.

Gratzel¹⁹ discusses three examples of suitable light-harvesting units which utilize metal complexes to capture photons and convert their energy to storable chemical fuel. The first two units consist of colloidal semiconductors and are more efficient than the third unit. The third, and most fundamental unit, comprises the sensitizer/relay pair. This unit, however, has poor efficiency because the area in which light induced charge separation and redox catalysis occurs, is not confined in a concentrated area.

In its most basic form, the unit consist of a sensitizer (S) and a relay (R), Figure 1.5. The illustration shows no spontaneous electron transfer occurring between the two species, S and R in the ground state. Upon excitation however, the sensitizer becomes virtually a new molecule with respect to the corresponding ground state thus exhibits different chemical properties. The sensitizer can then diffuse to an electron relay forming the precursor $S^* \cdots R$. During this encounter, electron transfer may occur forming the successor $[S^+ \cdots R^-]$; at this stage a majority of the photon energy absorbed by S can be converted into chemical potential through the product ions S^+ and R^- , see equation 1.1. These ions can then convert raw materials into chemical fuel, as shown in Figure 1.5.



The electron transfer within the precursor, $[S^+ \cdots R^-]$ is governed by the Franck-Condon principle in which the nuclear positions and nuclear velocities remain essentially unchanged during the electronic transition.²⁰⁻²² The potential energy diagram, Figure 1.6, shows that there is an energy state where the precursor and successor have identical energies. At this point in the precursor/successor encounter, electron transfer occurs without violating the Franck-Condon principle. Upon electron transfer, the inner vibration coordinates of the molecules and the outer solvation sphere adjust to a nonequilibrium position. Consequently there is an expenditure of free energy of reorganization ΔG^*_λ in the system. ΔG^*_λ may be related to the rate constant of the electron transfer event by the equation 1.2.

$$(1.2) \quad K_t = \gamma_N K_{e1} \text{EXP} \{-\Delta G^*_\lambda / RT\}$$

In this equation, γ_N is the effective vibration frequency, K_{e1} is the electronic transmission coefficient, R is the universal gas constant and T is the temperature in Kelvins.

Furthermore, ΔG^*_λ , a kinetic parameter, can be related to the free energy, ΔG° , a thermodynamic parameter, for electronic transfer, by the Marcus-Hush equation 1.3.

$$(1.3) \quad \Delta G^*_\lambda = \Delta G^*_\lambda(o) [1 + \{\Delta G^\circ / 4 \Delta G^*_\lambda(o)\}]^2$$

Here, $\Delta G^*_\lambda(o)$ is the free energy of reorganization. The Marcus equation implies that the free-energy of activation is expected to

decrease (meaning the reaction rate increases) when the reaction is thermodynamically favored. There is a point, however, in which the rate decreases at even higher thermodynamic driving force; this is called the Marcus inverted region.²⁰

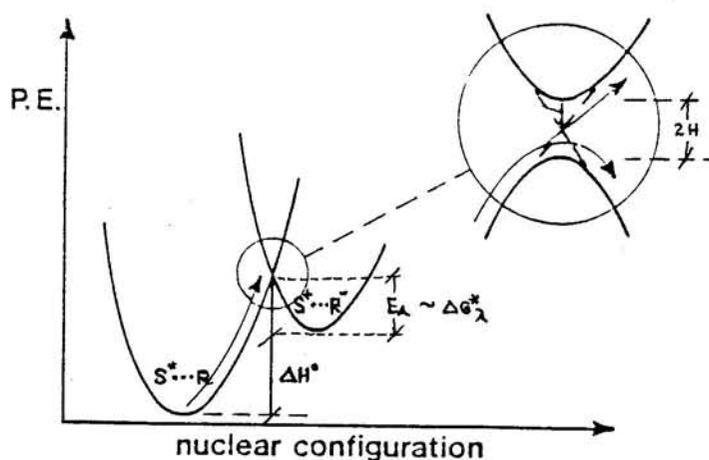


Figure 1.6

Classical model for electron-transfer process.^{6,19}

Electron transfer rates can be measured by Stern-Volmer quenching.^{23,24} Compounds which accept electrons are referred to as oxidative quenchers, and compounds which donate electrons are referred to as reductive quenchers. Table 1.2 lists some quenchers along with their redox potentials.²⁵⁻²⁸ By lifetime or emission intensity measurements of the excited state complex as it undergoes electron transfer with these quencher compounds, rates of electron

transfer can be calculated. For lifetime quenching the rate constant of electron transfer, k_q , may be determined from equation 1.4. A plot of $[1/\tau_o - 1/\tau_n]$ verses $[Q_n]$ leads to k_q .

$$(1.4) \quad [1/\tau_o - 1/\tau_n] = k_q [Q_n]$$

where, τ_o , is the lifetime of the complex with no quencher
 τ_n , is the lifetime of the complex for a given
concentration of quencher $[Q_n]$
 k_q , is the rate constant of electron transfer
 $[Q_n]$, is the quencher concentration

The excited state photoreducing and photo-oxidizing power ($*E_r^{\circ}$ and $*E_{ox}^{\circ}$) of the complex may be estimated by plotting k_q against the redox potential, E° , of the quencher. A quencher with small E° values (quenchers which easily donate or accept electrons) will have k_q values in the order of $\sim 10^9$. A k_q with this magnitude, is usually referred to as diffusion controlled; diffusion of the quencher to the excited state governs the rate of electron transfer. As the E° potential increases the electron transfer begins to be sluggish and the k_q drops below diffusion control. In other words, each encounter does not lead to electron transfer and a graph of E° vs. $\log k_q$ deviates from a straight line (with slope zero) and starts to break downward (as you will see in Figure 3.4.11). The E° potential at which the graph breaks is estimated to be the excited state redox potential.²⁹ The curvature of this graph also provide insights into the degree of structural distortion of the excited state.

TABLE 1.2

Redox Potentials of Oxidative and Reductive Quenchers (vs. NHE)

Oxidative Quenchers	-E°	Reductive Quenchers	E°.
pDNB p-dinitrobenzene	0.69	Pt phenothiazine	0.53
mDNB m-dinitrobenze	0.90	DMA N,N-dimethylaniline	0.81
NBA m-nitrobenzaldehyde	1.02	DPA diphenylamine	0.83
CNB p-chloronitrobenzene	1.06	AN aniline	0.98
NB nitrobenzene	1.15	TMB 1,2,4 trimethoxybenzene	1.12
MNB p-methylnitrobenzene	1.20	DMB 1,4 Dimethoxybenzene	1.34
pAN p-aminonitrobenzene	1.34	mTMB 1,3,5-trimethoxybenzene	1.49

In the past five years our group has synthesized and identified ortho-metalated complexes for use in photoconversion schemes. To this end, Dr. Kevin A. King was responsible for pioneering the work in ortho-metalated complexes.³⁰ During his tenure in the group, he prepared and characterized iridium dimers such as $[\text{Ir}(\text{NC})_2\text{Cl}]_2$ where NC = 2-phenylpyridine (ppy), or 7,8-benzoquinoline (bzq). From these dimers, he prepared complexes of the type $[\text{Ir}(\text{NC})_n\text{NN}_{3-n}]^{3-n}$ where NN is 2,2'-bipyridine, or 1,10-phenanthroline. He also

isolated the first Ir(III) ppy triply ortho-metalated complex, fac-Ir(ppy)₃. Ashley P. Wilde studied the excited state behavior of some of these iridium complexes.³¹ Dr. Steven Sprouse synthesized Rh analogues,³² while Dr. Carl A. Craig prepared the Pd and Pt analogues³³ with other ligands such as 2,(2-thienyl)pyridine, 2-phenylpyrimidine and ethylenediamine among those already mentioned. Craig also developed the synthetic scheme to couple mixed metal, mixed valence ortho-metalating complexes of the type [M(NC)Cl₂(NC)₂M'] where M is Pt, or Pd, NC is ppy or bzq, and M' is Rh(III). Dr. Peter Spellane prepared Re analogues, but his greatest asset to the group was his pioneering work in NMR spectroscopy to characterize the Ir, Ru, and Rh complexes of King and Sprouse.³⁴ The collaborative efforts by these individual have afforded fundamental understanding on the utility of ortho-metalated complexes as photosensitizer.

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Chapters 2 - 7

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of my dissertation

APPENDIX F

*I believe that we cannot live better
than in seeking to become still better
than we are.*
-Socrates

We've come to my favorite section of this dissertation. I just completed the dedication page found at the beginning (p iii). I feel that there are still many others I need to acknowledge. I know this section may seem unorthodox, but it is my thesis and I feel that this work would be incomplete without this last acknowledgment. (Besides, I do owe someone a pigeon section). These individuals are very much a part of this work because each has touched my life and in that way have contributed to this work.

I read somewhere (Trina Paulus, "Hope for the Flowers", — thanks for the book Pia) that someone once asked an artist how long it took him to make a certain picture. "*Five minutes and my whole lifetime,*" he responded. This dissertation is like that. I want to sincerely thank each who has given either to this work itself or to the lifetime that made it possible.

To my family (again)—Nieves, Joe, Noel, Lelian, Grace and Will. Thanks for always standing by my side, especially in difficult moments.

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trouble-maker son, 'specially when he no can keep his "s#!+".

Margi (Jim), thanks for making the third floor a pleasant place to
work. Your Big smile always somehow bring out the sunshine—even
in foggy days. Thanks also fo'— you know what fo'.

Dukie (Delphine), thanks for late-nite company on the NMR
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X's & O's.

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And to others I fear I forgot, sorry 'ey?

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A SCIENTIST CREED

Relying upon a faith that our
universe is not a chaos
but an ordered cosmos.

I believe that through sincere
and courageous efforts
man can learn what is true

I believe that inherent is what
is true is that which
will serve creation in its
highest form, which is Humanity.

I believe that truth shall
make man free—free from the
ills of the flesh and the spirit.

I rely upon an unfolding
knowledge of the truth to
provide a solution for the
problems and conflicts that
vex humanity.

I therefore dedicate
myself to the task
of seeking the truth
fearlessly and zealously,
and to the application
of what knowledge I
may gain for the
establishment of a
peaceful, just and
orderly civilization on
earth.

—Arthur H. Compton

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DO NOT WRITE ABOVE THIS LINE. IF YOU NEED MORE SPACE, USE A SEPARATE CONTINUATION SHEET.

PREVIOUS REGISTRATION Has registration for this work, or for an earlier version of this work, already been made in the Copyright office?

- Yes No If your answer is "Yes," why is another registration being sought? (Check appropriate box) ▼
- This is the first published edition of a work previously registered in unpublished form.
- This is the first application submitted by this author as copyright claimant.
- This is a changed version of the work, as shown by space 6 on this application.

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If your answer is "Yes," give: Previous Registration Number ▼ Year of Registration ▼

DERIVATIVE WORK OR COMPILATION Complete both space 6a & 6b for a derivative work; complete only 6b for a compilation.

a. Preexisting Material Identify any preexisting work or works that this work is based on or incorporates. ▼

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b. Material Added to This Work Give a brief, general statement of the material that has been added to this work and in which copyright is claimed. ▼

See instructions before completing this space.

MANUFACTURERS AND LOCATIONS If this is a published work consisting preponderantly of nondramatic literary material in English, the law may require that the copies be manufactured in the United States or Canada for full protection. If so, the names of the manufacturers who performed certain processes, and the places where these processes were performed must be given. See instructions for details.

Names of Manufacturers ▼ **UNIVERSITY MICROFILMS INC.**
Places of Manufacture ▼ **ANN ARBOR, MICHIGAN 48106**

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REPRODUCTION FOR USE OF BLIND OR PHYSICALLY HANDICAPPED INDIVIDUALS A signature on this form at space 10, and a check in one of the boxes here in space 8, constitutes a non-exclusive grant of permission to the library of Congress to reproduce and distribute solely for the blind and physically handicapped and under the conditions and limitations prescribed by the regulations of the Copyright Office: (1) copies of the work identified in space 1 of this application in Braille (or similar tactile symbols); or (2) phonorecords embodying a fixation of a reading of that work; or (3) both.

- a Copies and Phonorecords
- b Copies Only
- c Phonorecords Only

See instructions.

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DEPOSIT ACCOUNT If the registration fee is to be charged to a Deposit Account established in the Copyright Office, give name and number of Account.

Name ▼ **UNIVERSITY MICROFILMS INC.**
Account Number ▼ **DAO 64793**

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CORRESPONDENCE Give name and address to which correspondence about this application should be sent. Name/Address/Apt/City/State/Zip ▼

**UNIVERSITY MICROFILMS INC.
300 NORTH ZEEB RD.
ANN ARBOR MICHIGAN 48106**

Area Code & Telephone Number ▶ **313-761-4700**

Be sure to give your daytime phone number.

CERTIFICATION I, the undersigned, hereby certify that I am the

- Check one ▶
- author
 - other copyright claimant
 - owner of exclusive right(s)
 - authorized agent of **GARCES, FRED OMEGA**

of the work identified in this application and that the statements made by me in this application are correct to the best of my knowledge.

Name of author or other copyright claimant, or owner of exclusive right(s) ▲

Typed or printed name and date ▼ If this is a published work, this date must be the same as or later than the date of publication given in space 3.

PATRICIA L. MARTELL date ▶ **11/21/89**

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Handwritten signature (X) ▼

Patricia L. Martell

MAIL CERTIFICATE TO

Name ▼	GARCES, FRED OMEGA
Number/Street/Apartment Number ▼	CHEMISTRY DEPT., COLUMBIA UNIVERSITY
City/State/Zip ▼	NEW YORK, NY 10065

Certificate will be mailed in window envelope

- Have you:
- Completed all necessary spaces?
 - Signed your application in space 10?
 - Enclosed check or money order for \$10 payable to Register of Copyrights?
 - Enclosed your deposit material with the application and fee?

MAIL TO: Register of Copyrights, Library of Congress, Washington, D.C. 20559

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§17U.S.C. 506(e). Any person who knowingly makes a false representation of a material fact in the application for copyright registration provided for by section 409, or in any written statement filed in connection with the application, shall be fined not more than \$2,500.

