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CYCLOMETALLATED AND CYCLOMETALSILYLATED COMPLEXES OF
TRANSITION ELEMENTS AS PHOTOREDOX SENSITIZERS

Progress Report for the Period
December 1, 1991 - September 30, 1992

and

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I. Progress Report, 12/1/91 - 10/30/92

1. Metal-Silicon Chelated Complexes.

The initial efforts to synthesize and characterize tris chelates of 8-diorganosilylquinolines resulted in the isolation and identification of several such species with either Ir(III) or Rh(III) metal centers. Accounts of the initial synthetic and structural work have now been published^{1,2}, and efforts in this area are now being directed primarily toward spectroscopic and photochemical characterizations of these materials. The three primary structural types being researched in this effort are illustrated in Figure 1 below.

Figure 1. Structures of tris-N,Si-Chelated Ir(III) Complexes

Structurally analogous complexes of two the three types illustrated above for Ir(III) have also been isolated as Rh(III) derivatives. In addition, several Ir(III) and Rh(III) derivatives in which an isopropyl substituent is present on the phenyl ring of the quinoline ligand have been characterized. These later derivatives have markedly enhanced solubilities in a variety of non-polar organic solvents. Due to the presence of dissymmetric Si centers as well as the dissymmetric metal center in complexes of the 8-phenyl-methylsilylquinoline ligand (see $\text{Ir}(\text{pmsq})_3$ above), four different diastereomers of this complex are possible, each of which would be formed as a racemic mixture of enantiomers. We have succeeded in isolating three of these four diastereomers for the Ir(III) complex and two of the four for the Rh(III) complex. These will be characterized by a variety of spectroscopic methods in order to clarify what effects the subtle structure variations might have upon the excited state reactivities of these metal complexes.

Initial characterizations of the excited states of the three structural types illustrated in Figure 1 have been completed, and the results of the study are compiled in Table I on the following page. The diastereomer of the 8-phenyl-

TABLE I

Complex	Luminescence τ^a				Q^b	τ/Q^c	Emission λ^d	Assignment ^e
	77 K (μ s)		298 K (ns)					
	MeTHF	3MP	MeTHF	Tol				
Ir(dmiprSign) ₃	39	28	310	980	0.010	98	600	$\sigma\text{-}\pi^*$ (SBLCT)
Ir(pmiprSign) ₃	71	52	400	850	0.027	33	550	$\sigma\text{-}\pi^*$ (SBLCT)
Ir(dpiprSign) ₃	200	172	—	201	0.001	201	510	$\sigma\text{-}\pi^*/\pi\text{-}\pi^*$
Rh(dmiprSign) ₃	540	420	—	38	—	—	590	$\sigma\text{-}\pi^*$ (SBLCT)
Rh(dmSign) ₃	360	—	—	—	—	—	590	$\sigma\text{-}\pi^*$ (SBLCT)
Rh(pmSign) ₃	1400	—	—	—	—	—	590	$\sigma\text{-}\pi^*$ (SBLCT)

a. Emission lifetime.

b. Emission quantum yield in toluene at 298 K.

c. Radiative lifetime (μ s) in toluene at 298 K.

d. Wavelength (nm) at maximum of emission spectrum in MeTHF at 77 K.

e. SBLCT = sigma-bond-to-ligand charge-transfer.

Abbreviations

MeTHF = 2-methyltetrahydrofuran

3MP = 3-methylpentane

tol = toluene

dmiprSign = 8-dimethyl-6-isopropylsilylquinolyl

pmiprSign = 8-phenylmethyl-6-isopropylsilylquinolyl

dpiprSign = 8-diphenyl-6-isopropylsilylquinolyl

dmSign = 8-dimethylsilylquinolyl

pmSign = 8-phenylmethylsilylquinolyl

methyilsilylquinoline complex which has been studied in all cases thus far is the Δ RRR, Δ SSS racemic mixture, which is the primary product formed in the synthetic procedures we have utilized. The excited states in these complexes are assigned largely as sigma-bond-to-ligand charge transfer (SBLCT) as a result of their long radiative lifetimes and spectral shifts in their energies with changes in solvent polarity. The simple molecular orbital model used in describing these transitions is illustrated in Figure 2 below. This model is based upon the assumption that the energy of the Si sigma-donor orbitals is comparable to the energy of the metal d-sigma acceptor orbitals, leading to a highly covalent M-Si bonded structure. SBLCT excited states are expected to

Figure 2. Orbital Transitions in 8-Diorganosilyl(Quinoly) M(III) Complexes

become progressively more dominant as metal centers are bound to C, Si, Ge, and Sn, and it is indeed the case that several SBLCT transitions have been assigned to excited states in Re-Sn and Re-Ge bonded complexes.^{3,4}

The presence of low-lying SBLCT excited states in these complexes raises interesting possibilities for the photochemistry in which they might participate. Since the promotion of a sigma-bonding electron into a ligand pi* orbital should substantially weaken the M-Si bond, a strong tendency to cleave the bond and to open a coordination site is anticipated (See Figure 3). The transient diradical postulated to result from M-Si bond cleavage following excitation would be expected to be highly reactive. Figure 3 illustrates that such a diradical might, for example, abstract a proton from

Figure 3. Possible Photoreactivity of SBLCT Excited States

a solvent and coordinate the solvent anion prior to returning to the starting material. The remarkable shortening of the excited state lifetime in fluid 2-methyltetrahydrofuran relative to toluene for all of the complexes we have studied (See Table I), for example, may be indicative of this type of reactivity pattern.

In order to explore further the nature and reactivity of excited states in these complexes, an apparatus designed to monitor time-resolved excited state absorption spectra and absorption of transients in the 10 ns - 100 ms time domain has been fully developed. This apparatus employs a relatively low-powered nitrogen laser (6 mJ/pulse) as a pump source at 337 nm, and a nitrogen nanopulse flash lamp as an analyzing probe. Time resolution is achieved by adjusting the delay time between pump and probe pulses with a trigger delay generator and monitoring the probe both with and without excitation by the pump with a 512 element diode array. A schematic diagram of this apparatus is shown in Figure 4 with an example of the well-known differential absorbance spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ which is generated in order to check the optical alignment and electronic timing of the apparatus.

The present emphasis in this project is being placed on characterizations of the time-resolved differential absorbance characteristics of M-Si bonded complexes in several different solvent systems. The study is being started with the most inert solvents which can adequately solubilize the complexes for the transient absorption measurements.

Figure 4. Apparatus for Time-Resolved Transient Absorption Measurements

Initial time-resolved differential absorbance characterizations of two Ir-Si bonded complexes in toluene are illustrated in Figure 5. Both sets of absorbance changes illustrate that formation of the excited state is accompanied by bleaching of the absorption bands in the 350 - 450 nm region as well as formation of two new absorption bands which span most of the visible region, 450 - 750 nm. Bleaching of the 350 - 450 nm bands is consistent with assignment of these bands to SBLCT transitions which lose intensity when a sigma-bonding electron is transferred. At this point, it appears likely that the new visible bands are associated with the quinoline radical anion which results from the transfer of charge to quinoline. In both cases, disappearance of the new absorption bands occurs on the same time scale as the emission decay, further indicating that these bands are associated with the excited state. Whereas the bleaching also disappears on the same time scale as the emission decay in the dimethyl derivative, the phenylmethyl derivative deviates significantly from this behavior. In this later case, the bleaching increases over a period of several hundred ns, and then begins to gradually decrease. This is thought to be

Figure 5. Time-Resolved Differential Absorption Spectra of $\text{Ir}(\text{N,Si})_3$ in Deoxygenated Toluene at 298 K
 (A) N,Si = 8-dimethylsilyl-6-isopropylquinolyl
 (B) N,Si = 8-phenylmethyl-6-isopropylquinolyl

characteristic of a transient species associated with cleavage of an Ir-Si bond. Since the excited state absorption is disappearing as this bleaching grows, the transient is one in which the electron no longer resides upon the quinoline. Thus, the transient responsible for this bleaching might be one in which a metal-silicon bond has cleaved and a solvent molecule has been reduced and perhaps coordinated by the metal center as illustrated in Figure 3.

This project is moving quite rapidly at the present time, and subsequent to completion of characterizations of the transient species formed following laser flash photolysis in "inert" solvents, we will begin to explore the chemical reactivity of these transients with added substrates. Of particular interest for these studies will be carbon-containing substrates such as CO_2 and CO , proton sources such as gaseous HCl , and coordinating solvents such as acetonitrile. In each instance, a combination of transient absorption analysis and continuous wave irradiation with product analysis will be employed to clarify the nature of the photo-reactivity of these M-Si bonded chelates.

2. Photoproperties of Ortho-metalated Complexes.

Our recent work in this area has included collaborative efforts with Professor Keith DeArmond at New Mexico State University and with Professor F. Kirsch-De Mesmaeker at the Free University of Brussels in Belgium. The former project has employed tris ortho-metalated Ir(III) complexes as luminescent and electrochemical probes in Langmuir-Blodgett films, and the work has resulted in preparation of a manuscript which has been submitted for publication.⁵ In the latter project, ortho-metalated Ir(ppy)₂- fragments are being attached to bridging hexazatriphenylene (HAT) and tetrazaphenanthrene (TAP) ligands which contain Ru(bpy)₂- fragments bound at other sites. The eventual goal of this work is to induce long-range electron transfer from the Ir(ppy)₂ sites through the bridging HAT or TAP ligands to the Ru(bpy)₂ sites. A manuscript describing some of the initial studies in this project is presently being prepared.

The characterizations of the low temperature emission spectroscopy and room temperature ground state and excited state absorption spectroscopy of a series of complexes of the type [Ru(X-ppy)(bpy)₂]⁺ (X=fluoro, n-propyl, t-butyl, or H) has recently been completed. The X = nitro derivative was studied and reported some time ago,^{6,7} for its emission and electrochemical properties. That derivative is stabilized by the strongly electron withdrawing nitro substituent, and we have sought to characterize derivatives which are more sensitive to oxidation and which have much lower energy MLCT excited states than the nitro-substituted derivative. The results of this study are summarized in Table II and Figure 6 below.

Although a very weak emission can be monitored for the complexes in room temperature acetonitrile, both emission and excited state absorption attempts to monitor the excited state lifetimes indicate that they are less than the time resolution abilities of our apparatus (< 20 ns). The ground state and excited state absorption results illustrated in Figure 6 are consistent with strongly absorbing MLCT transitions throughout the visible in the ground state. These transitions are strongly bleached in the excited state and the absorption around 390 nm is enhanced due to formation of the bipyridine radical anion.

TABLE II

<u>Complex</u>	<u>Luminescence τ (ns)^a</u>	<u>Emission λ (nm)^b</u>	<u>Assignment^c</u>
$[\text{Ru}(\text{ppy})(\text{bpy})_2]^+$	290	738	MLCT
$[\text{Ru}(\text{n-propylppy})(\text{bpy})_2]^+$	250	740	MLCT
$[\text{Ru}(\text{t-butylppy})(\text{bpy})_2]^+$	230	742	MLCT
$[\text{Ru}(\text{fluoroppy})(\text{bpy})_2]^+$	890	698	MLCT

- a. Luminescence lifetime of complex at 77 K in 4/1 ethanol/methanol.
 b. Emission maximum of complex at 77 K in 4/1 ethanol/methanol.
 c. In all cases bpy is the accepting ligand in MLCT from Ru(II).

Figure 6. Ground State Absorption and Time-Resolved Difference Spectra of Ru(II) Complexes in Acetonitrile at 298 K
 (A) $\text{Ru}(\text{F-ppy})(\text{bpy})_2^+$ (B) $\text{Ru}(\text{ppy})(\text{bpy})_2^+$

II. Outline of Plans for 3/1/93 - 2/28/94.

1. Metal-Silicon Chelated Complexes.

Studies of complexes of this type will be the primary focal point of research in the forthcoming period. The initial work on characterization of the excited state and transient absorption spectra of these species in inert solvents has developed nicely, and this work will be continued during the forthcoming period. In particular, we will begin to study the temperature dependence of the luminescence lifetime and transient absorption characteristics in hopes of establishing whether there exists a well-defined temperature region where M-Si bond cleavage becomes apparent. The known change of lifetime from several hundreds of microseconds at 77 K to several hundreds of nanoseconds or even less in some solvents at 298 K is indicative of the type of major temperature effects which will be analyzed in detail. These studies will be performed for complexes of both Rh(III) and Ir(III) in hopes of establishing whether or not the central metal has a major influence upon M-Si bond cleavage in these species. The occurrence of both emission and transient photoactivity appears quite certain in room temperature solutions of several of these complexes, so we will have several methods to monitor both excited state decay processes and to differentiate these from photochemical transients formed from the emissive excited state. It is quite possible that these studies will serve to clarify the absorption characteristics of transient intermediates which might form rapidly due to M-Si bond cleavage but then yield intermediate products which decay slowly due to combined effects of low temperatures and viscous solvents.

The second aspect of this project which we shall begin to explore is the possible photo-induced reactivity of these complexes with added substrates such as CO_2 , CO, and ligating solvents such as acetonitrile. We have already discovered that most of the complexes are non-emissive in coordinating solvents such as acetonitrile, another indication of the likelihood of M-Si bond cleavage and insertion of a solvent into an open coordination site. It is a bit surprising that the solvent seems to promote the cleavage process and to completely quench the emission, and we will attempt to use transient absorption spectroscopy to clarify by what mechanism this quenching occurs. As CO is known to be a strongly ligating species toward these electron rich metal centers, we would like to establish whether CO completely blocks reformation of the M-Si bond once it is cleaved, or whether CO will undergo a net reaction to form a photoproduct. As our original intent in pursuing this type of chemistry was to seek electron rich materials which might be caused to undergo photoreactions to reduce CO_2 , we are particularly anxious to monitor the effects of added CO_2 in flash photolysis of these materials. At the present time it appears that sufficiently inert solvents can be found to avoid photoactivity with the

solvent medium with several of the complexes. For example, cyclohexane appears to be non-reactive, although we are quite limited by the few of the species we have prepared which are sufficiently soluble to perform a study in this solvent. Although toluene appears to be somewhat more reactive as a solvent medium, several complexes have thus far shown no particular reactivity with this solvent, so that it may prove to be of some use as an inert medium in which to monitor possible CO₂ reactivity.

A third aspect of this project which will be pursued during 1993-94 will be a study of the effects of diastereomeric structure changes on the excited states and photoactivities of several complexes of the 8-phenylmethylsilyl(quinoliny) ligand. As we have characterized several of these tris complexes of both Ir(III) and Rh(III), the difficult synthetic and structural work is well underway. We will now begin to monitor both emission and excited state absorption characteristics of these species, as well as the absorption transients which are seen following pulsed excitation. These may prove to be of particular interest both for the influence of diastereomeric structure upon the nature of their excited states and for its influence upon photoreactivity. The relative location of methyl and phenyl groups in the structure of these species could have a major effect upon the manner in which a reactive substrate might enter the coordination sphere of the central metal subsequent to M-Si bond cleavage. Thus, a combination of electronic and steric effects might greatly influence changes in photoreactivity between different diastereomers.

The final aspect of this project which will be pursued in 1993-94 will be in development of the M-Si chemistry of Pt(II) complexes. Initial work in this area was started this year, and starting materials and synthetic procedures appropriate for the project have been partially established. Several square planar Pt(II) complexes of our N,Si-chelates have been isolated and partial characterizations have been made. It will be necessary to complete these characterizations before the structures are known with an acceptable level of confidence, but the results appear to be promising thus far. These materials are of particular interest due to their potential ability to undergo oxidative addition reactions to form 6-coordinate Pt(IV) complexes. While oxidative addition chemistry is a well-known class of chemical reactivity for d⁸ species, this type of chemistry is but little known for Pt(II)-Si chelated materials.⁸ During the forthcoming period, our attention will be focussed upon structural and spectroscopic characterizations of these materials, in hopes that we will gain sufficient insight to eventually explore their possible participation in photo-induced oxidative addition and reductive elimination chemistry.

2. Photoproperties of Ortho-metalated Complexes.

With the successful characterization of several complexes of the type $[\text{Ru}(\text{X-ppy})(\text{bpy})_2]^+$ described above, we are now prepared to begin a study of the possible participation of these species in photo-induced electron transfer reactions. Whereas the well known $[\text{Ru}(\text{bpy})_3]^{2+}$ complex is known to be an equally good oxidizing and reducing agent in its MLCT excited state, these ortho-metalated species are far stronger reducing agents than they are oxidizing agents in their excited states. This property can be used to advantage, for example, by seeking to reductively quench the excited state to produce $\text{Ru}(\text{ppy})(\text{bpy})_2^0$, and then to utilize this as a two-electron reducing agent through the couple $[\text{Ru}(\text{ppy})(\text{bpy})_2]^{2+}/\text{Ru}(\text{ppy})(\text{bpy})_2^0$. Unlike the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex which generates very little potential due to the two electron couple, $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{1+}$, the ortho-metalated species will have a substantial potential in its two electron couple if the reductive quenching step can be accomplished.

A similar theme will be pursued with complexes of the type $\text{Ir}(\text{ppy})_3^0$. We have been exploring means by which these might be reductively quenched to yield the very powerful reducing agent, $[\text{Ir}(\text{ppy})_3]^{1-}$. While it does appear that the reductive quenching step has been successful in several instances, the resulting species is so reactive that we have thus far been unable to characterize it. This work will continue during the forthcoming period with an initial goal to find a medium and quencher in which the reduction can be done to produce an identifiable species. If this is achieved, we will then attempt to use this species to perform a one-electron reduction of CO_2 to CO_2^- prior to attempts to explore the two electron couple which it might provide.

III. Activities.

A. Publications

68. A New Class of Metal-Silicon Bonded Complexes: 8-(dimethylsilyl) Quinoline Derivatives of Rhodium and Iridium. P.I. Djurovich, A. Safir, N. Keder and R.J. Watts, Coord. Chem. Rev. **1991**, 111, 201.
69. Synthesis and Structure of fac-Tris[(8-quinolyl)dimethylsilyl] rhodium(III) and -Iridium(III). P.I. Djurovich, A.L. Safir, N.L. Keder and R.J. Watts, Inorg. Chem. **1992**, 31, 3195.
70. Ortho-metalated 2-(p-Tolyl)pyridine Iridium (III) Complexes. F.O. Garces, K. Dedeian, N.L. Keder and R.J. Watts, Acta Crystal. **submitted**.
71. Synthesis and Spectroscopic Properties of Ortho-Metalated Iridium(III) Solvento Complexes. B. Schmid and R.J. Watts, Inorg. Chem. **Submitted**.
72. Langmuir-Blodgett (LB) Films of Tris(2-phenylpyridine) Iridium(III). H.A. Samha, T.J. Martinez, M.K. DeArmond, F.O. Garces and R.J. Watts, Inorg. Chem. **Submitted**.
73. ^1H and ^{13}C NMR Assignments with Coordination-Induced Shift Calculations of Carbon σ -Bonded Ortho-Metalated Rhodium(III) and Iridium(III) Complexes. F.O. Garces and R.J. Watts, Mag. Res. in Chem. **Submitted**.

B. Professional Activities

"Chelate-Assisted Hydrosilylation: Nitrogen vs. Phosphorus Coordination at Iridium" P.I. Djurovich, A. Safir, N. Keder, W. Harrison and R.J. Watts, 25th Silicon Symposium, Los Angeles, CA, April 3-4, 1992.

"Solvent Viscosity and Temperature Effects on Interligand Electron Hopping in Ortho-Metalated Complexes of Ir(III)" C.M. Miller and R.J. Watts, 203rd National ACS Meeting, San Francisco, CA, April 5-10, 1992.

"MLCT Tuning: Synthesis, Characterization, and Photophysics of Substituted Phenylpyridine Ortho-metalated Iridium (III) Dimers" G.A. Carlson, E. Hagen, P.I. Djurovich and R.J. Watts, 203rd National ACS Meeting, San Francisco, CA, April 5-10, 1992.

"Sigma-Bond-To-Ligand Charge-Transfer (SBLCT): Spectroscopic Studies of 8-(Diorganosilyl)quinolyl Derivatives of Rhodium(III) and Iridium(III)" P.I. Djurovich, A. Safir, N. Keder, B. Harrison, J. Green and R.J. Watts, 203rd National ACS Meeting, San Francisco, CA, April 5-10, 1992.

"Recent Developments in the Photoproperties of Metal-Carbon and Metal-Silicon Bonded Complexes" P.I. Djurovich, G.A. Carlson, F.O. Garces, C.M. Miller and R.J. Watts, Sixteenth DOE Solar Photochemistry Research Conference, Lake Geneva, WI, May 31 - June 4, 1992.

"Photophysical Properties of Metal-Silicon Bonded Complexes: 8-(Diorganosilyl)quinolyl Derivatives of Rhodium(III) and Iridium(III)" P.I. Djurovich, A. Safir and R.J. Watts, XIV IUPAC Symposium on Photochemistry, Leuven, Belgium, July 19-25, 1992.

"Spectroscopy and Photophysics of Ortho-metalated Iridium (III) Phenylpyridine Dimers and Mixed Ligand Monomers" G.A. Carlson, E. Hagen, P.I. Djurovich and R.J. Watts, 204th National ACS Meeting, Washington, D.C., August 23-28, 1992.

"Photophysical Properties of Metal-Silicon Bonded Complexes: 8-(Diorganosilyl)Quinolyl Derivatives of Rhodium (III) and Iridium (III)" P.I. Djurovich, A. Safir and R.J. Watts, 48th Southwest Regional ACS Meeting, Southwest Luminescence Symposium I: Theory, Dynamics and Applications, Lubbock, Texas, October 21-23, 1992.

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