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A NEW CLASS OF METAL-SILICON BONDED COMPLEXES: 8-(DIMETHYLSILYL) QUINOLINE DERIVATIVES OF RHODIUM AND IRIDIUM

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Abstract

Chelating ligands based upon 8-(dimethylsilyl)quinoline have been synthesized and used to prepare complexes of Rh(III) and Ir(III) in which the ligand coordinates the metal through a combination of M-N and M-Si linkages. These types of complexes have been formed via oxidative addition of the Rh(I) or Ir(I) precursors across either an Si-H or Si-Si bond of the N,Si-chelating ligand, and both bis- and tris-chelated species have been characterized. We report here the first photophysical characterizations of this new class of complexes. Their photophysical properties suggest that substantial modifications, relative to ortho-metalated species, occur as a result of the highly covalent nature of M-Si bonds as compared to M-C bonds.

I. INTRODUCTION

The design of inorganic photosensitizers has primarily involved the use of ligands that chelate a metal through two or more nitrogen atoms. Well-known examples are those based upon 2,2′-bipyridine and its derivatives, in combination with a Ru(II) central metal ion (1). These photosensitizers are noted for their ability to act as either moderately strong oxidizing or reducing agents in their luminescent excited states (*Ru(II)-(bpy)) as well as in the oxidized (Ru(III)-bpy) or reduced (Ru(II)-bpy$^-$) products formed in redox quenching of (*Ru(II)-bpy) (2). Several other classes of inorganic complexes have also been shown to hold promise as photoredox sensitizers (3), including those which contain cyclometallated ligands (4-6). This latter class of complexes, for which 2-

phenylpyridine (ppy) may be regarded as a prototypical ortho-metalating ligand, are much weaker oxidizing agents but far stronger reducing agents than comparable complexes of 2,2′-bipyridine. For example, $Ir(bpy)_3^{3+}$, is among the strongest of the known photo-oxidants while fac-$Ir(ppy)_3$ is one of the strongest of the known photoreductants (4a,7).

These profound effects of metal-carbon bonding on the photoredox properties of Ir(III) have led us to begin studies of a new class of complexes in which the central metal ion is chelated by ligands through a combination of metal-nitrogen and metal-silicon bonds. The fundamental periodic trend toward lower ionization energy in moving down a column suggests that a metal-silicon bond might be an even stronger sigma-donor than is the metal-carbon bond. This might lead to even stronger photoreductants than those based upon ortho-metalated structures. However, a number of other complicating factors might come into play. a) Whereas carbon readily participates in sp^2 hybridization in planar aromatic ring systems which may be bonded to metal centers via ortho-metalation, silicon is noted for it's strong preference towards sp^3 hybrids and related non-participation in aromatic ring structures. b) Back-bonding may occur in ortho-metalated structures through the empty pi^*-orbitals of an aromatic ring system of an sp^2 hybridized carbon atom which is sigma-bonded to a metal, but the 3-d orbitals of carbon are generally neglected due to their high energy. An sp^3 hybridized silicon is more likely to participate in pi-backbonding through its empty 3-d orbitals which are energetically more accessible. However, recent studies have raised questions regarding whether or not any strong evidence has been found for pi-back-bonding effects in metal silyls (8). c) Some degree of covalency is anticipated in the metal-carbon sigma bonds in ortho-metalated species, and this might be substantially increased in metal-silicon sigma-bonded structures.

While there have been no reports of the photophysical properties of N,Si-chelated species prior to this work, a definitive series of papers on the chemistry and structural characterization of P,Si-chelated species have been published by Stobart, et al (9). The P,Si-chelating ligands have been found to oxidatively add to a variety of low-valent metal centers (the term "chelate-assisted hydrosilylation" (9) has been coined to describe this process), and the resulting 5-membered metallocycle stabilizes the complex toward loss, via reductive elimination, of the Si-binding ligand.

We have set out to design silyl ligands which combine the stabilizing effects of previously studied P,Si-chelating ligands with the ability of N-binding heterocyclic ligands to act as electron acceptors in promoting low-energy metal-to-ligand charge-transfer (MLCT) transitions. Once designed and prepared, these ligands have been used to prepare several complexes of Ir(III) and Rh(III) that serve to illustrate the types of modifications of the photophysical properties of M-C bonded (ortho-metalated) species which may be brought about in M-Si bonded species.

II. DESIGN AND PREPARATION OF N,Si-BINDING LIGANDS

The well-established ability of ligands containing the pyridine moiety to act as both strong sigma-donors through the N-atom and good electron acceptors through the empty pi* ring orbitals, led us to seek chelating ligands which would bind metals through a combination of N,Si-binding sites in which the N-binding site is within a pyridine-like ring. Furthermore, extension of the conjugated pi system through fused aromatic rings, as in the quinoline moiety, is known to promote low-energy MLCT. The choice of a fused ring system such as quinoline rather than a bridged system as in 2-phenylpyridine is dictated by the difficulty in preparing aromatic ring systems which would include an sp^2 hybridized Si atom. Given these considerations, 8-(dimethylsilyl)quinoline (mesiqn-H, Fig 1a), was prepared via lithiation of 8-bromoquinoline fol-

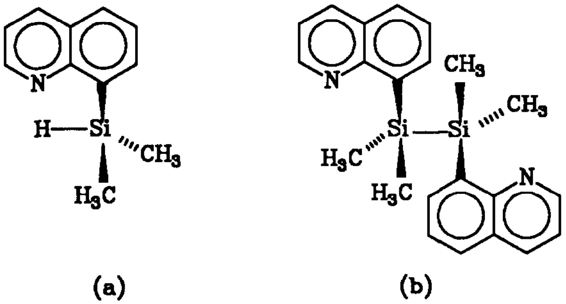
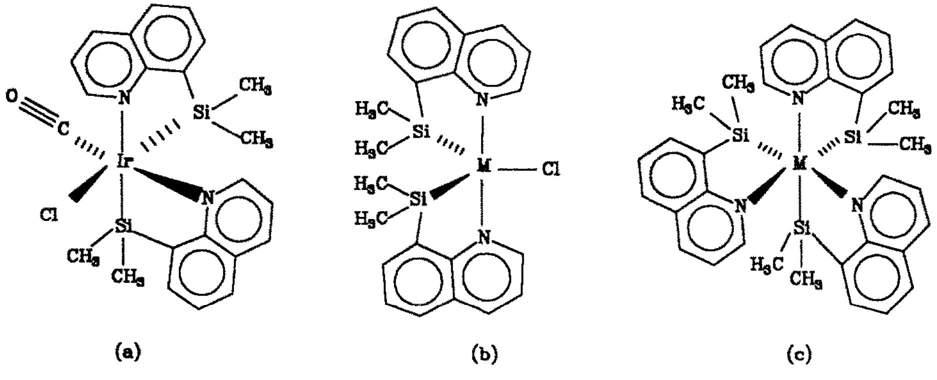


Figure 1. Structures of N,Si-chelating ligands. a) mesiqn-H) b) bis-mesiqn.

lowed by coupling to dimethylchlorosilane. Similarly, 1,2-bis(8-quinoline)tetramethyldisilane (bis-mesiqn, Fig 1b) was prepared via coupling of 1,2-dichlorotetramethyldisilane with the lithiated derivative of 8-bromoquinoline. While mesiqn-H was designed to react with metals via oxidative addition across a Si-H bond and N-coordination to form an N,Si-chelated metal hydride (10), bis-mesiqn was designed to avoid hydride formation via possible oxidative addition to a metal across the Si-Si bond (11,12) with cleavage of the ligand and formation of a *bis*-N,Si-chelated metal complex.

III. CHARACTERIZATIONS OF N,Si-CHELATED METAL COMPLEXES

Reactions of bis-mesiqn with several Ir(I) and Rh(I) starting materials has generally been found to yield either 5- or 6-coordinate *bis*-N,Si-chelated complexes of Ir(III) or Rh(III). A route for preparation of *tris*-N,Si-chelated complexes of both Ir(III) and Rh(III) via reaction of mesiqn-H with an appropriate Ir(I) or Rh(I) precursor has also been found. In contrast, although a successful synthetic route to *tris*-ortho-metalated complexes of Ir(III) is known (13), analogous procedures fail to yield *tris* ortho-metalated complexes of Rh(III). Structures of representative examples of both 5- and 6-coordinate N,Si-chelated complexes which have been prepared and studied are illustrated in Figure 2.



(a) (b) (c)

Figure 2. Structures of N,Si-chelated metal complexes.
a) Ir(mesiqn)$_2$(CO)(Cl) b) M(mesiqn)$_2$Cl (M=Ir, Rh)
c) M(mesiqn)$_3$ (M=Ir, Rh).

The complex, Ir(mesiqn)$_2$(CO)(Cl), was prepared by reaction of bis-mesiqn with [Ir(COD)Cl]$_2$ in refluxing 2-ethoxyethanol. The coordinated CO apparently originates via reaction of a reactive intermediate with the solvent; the structure of the final product was established by X-ray crystallography, ^{1}H, ^{13}C, ^{29}Si NMR, FTIR and MS (Fig 2a). The coordination environment around the metal center is pseudooctahedral with a cis,cis arrangement of both the nitrogens and the silicons of the mesiqn ligands, and with the chloride trans to the silicon of one mesiqn ligand while the carbonyl group is trans to the nitrogen of the other mesiqn ligand. This geometry suggests that M-Si bonds, like M-C bonds in ortho-metalated species, tend to be strong trans-directors.

When reaction of bis-mesiqn with [Ir(COD)Cl]$_2$ is carried out in refluxing ethanol rather than 2-ethoxyethanol, and the resulting precipitate is solubilized in pyridine/dichloromethane, a different product is obtained. Characterizations by ^{1}H NMR and MS analysis indicate that it is a monomeric 5-coordinate bis-mesiqn species in which chloride occupies a fifth coordination site. Since the only other reported 5-coordinate bis-chelated silyl iridium complex has a trigonal pyramidal structure with equatorial silicons and chloride (9e), we presume that Ir(mesiqn)$_2$Cl has a similar structure (Fig 2b). When [Rh(COD)Cl]$_2$ is used as a starting material in an otherwise similar reaction procedure, an analogous product, Rh(mesiqn)$_2$Cl, is isolated; the ^{1}H NMR is nearly identical to that of Ir(mesiqn)$_2$Cl, and it is also presumed to have the structure shown in Fig 2b.

Reaction of mesiqn-H with M(P(Ph$_3$)$_3$)(CO)(H) in toluene, (M = Ir(I) or Rh(I)), yields fac-M(mesiqn)$_3$ (M = Ir(III) or Rh(III)). The geometry of these complexes (Fig 2c) has been confirmed by ^{1}H, ^{29}Si NMR and X-ray crystallography . This is consistent with the presumed trans-directing effect of M-Si bonds which favors a mutually cis arrangement of the three M-Si bonds in the fac isomer over the mer isomer in which two M-Si bonds would occupy positions trans to one another.

IV. PHOTOPHYSICAL CHARACTERIZATIONS

Ir(mesiqn)$_2$(CO)Cl). The absorption spectrum of the complex (Fig 3) displays a band around 320 nm that is characteristic of the pi-pi* absorption seen in quinoline (14) and in the uncomplexed mesiqn-H ligand. The absence of added visible/uv

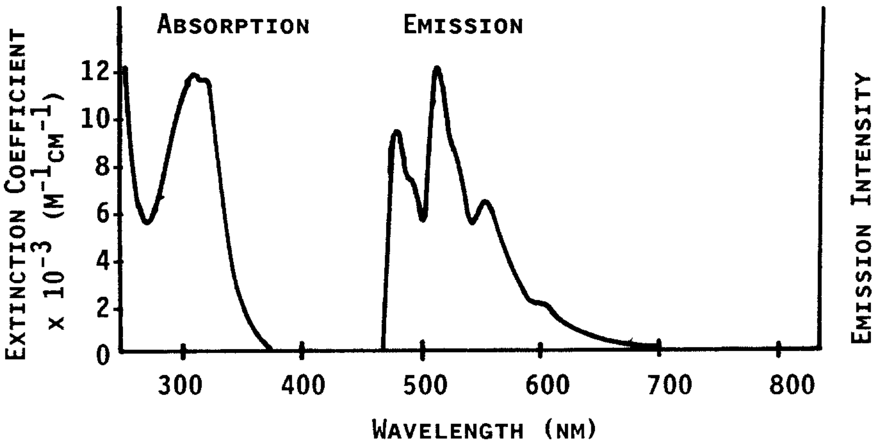


Figure 3. Absorption (298 K) and Emission (77 K) Spectra of Ir(mesiqn)$_2$(Cl)(CO) in 2-Methyltetrahydrofuran.

absorption features in this complex indicates that no low energy MLCT transitions result from complexation of the ligand to the Ir(III) metal center when CO is also present in the coordination sphere. Although no emission has been observed from fluid solutions of the complex, a strong, highly structured emission is observed from glassy 2-methyltetrahydrofuran solutions at 77 K (Fig 3). This is similiar in shape to the phosphorescence of quinoline (14) though it is shifted to the red by approximately 20 nm. The long lifetime of this emission (> 1 ms) is indicative of a pi-pi* excited state localized largely in the quinoline ring system.

Ir(mesiqn)$_2$Cl and fac-Ir(mesiqn)$_3$. The main features in both the absorption and emission spectra of these two complexes (Fig 4) are similar to one another, but quite distinct from the features seen in the absorption and emission of Ir(mesiqn)$_2$(CO)(Cl). Two new absorption features are seen: a shoulder at about 440 nm and a well-resolved peak at 360-370 nm. The extinction coefficient of the shoulder at 470 nm is nearly the same for the two complexes (4 x 10^3 M^{-1}cm^{-1}), but the band at 360-370 nm is nearly twice as intense in Ir(mesiqn)$_2$Cl (1.2 x 10^4 M^{-1}cm^{-1}) as it is in _fac_-Ir(mesiqn)$_3$ (6 x 10^3 M^{-1}cm^{-1}). Both complexes display a third, well-resolved band at about 310 nm which is similar in position and in intensity to the quinoline-like transition of Ir(mesiqn)$_2$-(CO)(Cl). The absorption spectrum of _fac_-Ir(mesiqn)$_3$ has been

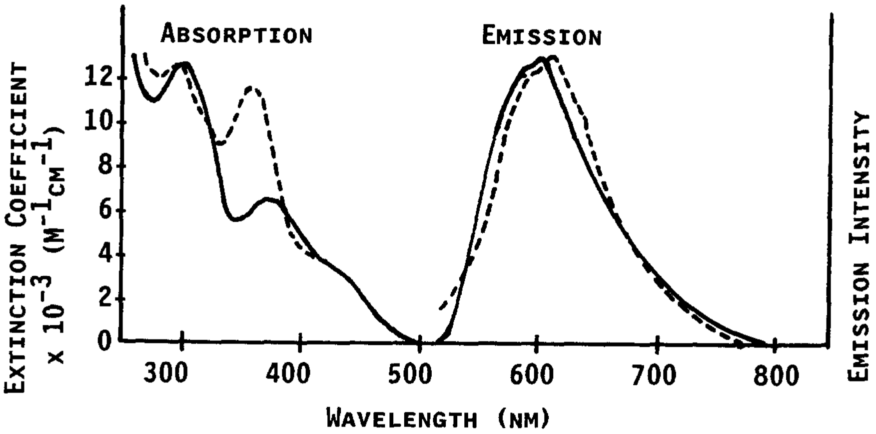


Figure 4. Absorption (298 K) and Emission (77 K) Spectra of $Ir(mesiqn)_3$ (———) and $Ir(mesiqn)_2Cl$ (- - -).

monitored in several solvents, and the two low energy absorption features are found to blue shift substantially as the polarity of the solvent increases.

Both complexes display broad, strong emissions centered at about 600 - 610 nm in glassy 2-methyltetrahydrofuran solutions at 77 K (Fig 4). Although no emission is observable from fluid solutions of the bis complex, $Ir(mesiqn)_3$ continues to emit strongly in fluid 2-methyltetrahydrofuran solutions with very little change in the shape or position of the emission spectrum relative to the 77 K spectrum. The lifetime of the $Ir(mesiqn)_3$ emission is 28 us at 77 K and it shortens to about 2.1 us in deoxygenated 2-methylpentane solutions at ambient temperature.

fac-$Rh(mesiqn)_3$ and $Rh(mesiqn)_2Cl$. The absorption spectra of these two complexes (Fig 5) are again similar to one another as well as to the two corresponding complexes of Ir(III) described above, save for the absence of the low energy shoulders in the region around 440 nm. As in the two Ir(III) complexes, the intensity of the $Rh(mesiqn)_2Cl$ absorption at 360 nm (1.2 x 10^4 $M^{-1}cm^{-1}$) is roughly twice that of $Rh(mesiqn)_3$.

The emission spectra of these two Rh(III) complexes also closely parallel the emission behavior of the two Ir(III) complexes. Glassy 2-methyltetrahydrofuran solutions of each complex at 77 K yield broad emission spectra centered at about 580 - 600 nm (Fig 5). In fluid solutions at room temperature,

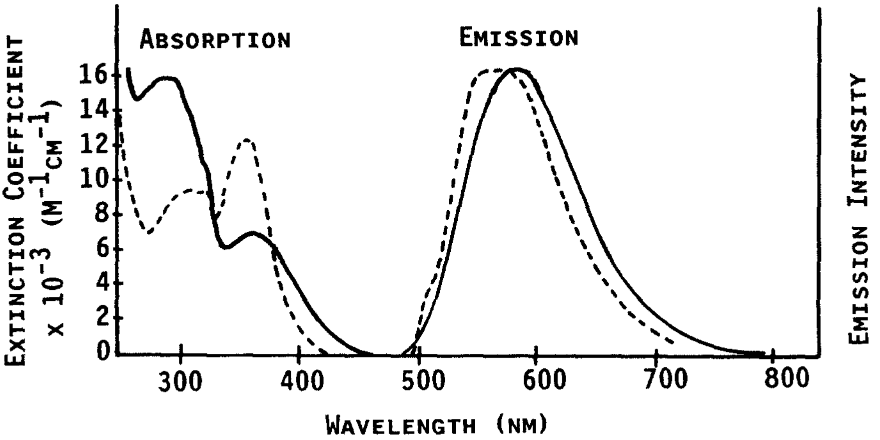


Figure 5. Absorption (298 K) and Emission (77 K) Spectra of Rh(mesiqn)$_3$ (———) and Rh(mesiqn)$_2$Cl (- - -).

no emission is observable from the 5-coordinate complex, but fac-Rh(mesiqn)$_3$ displays a weak emission which is very similar in shape and position to the emission at 77 K. The lifetime of emission at 77 K is 300 us, and this is shortened substantially to about 70 ns in deoxygenated fluid solutions at room temperature.

V. DISCUSSION AND SUMMARY

The chemistry and photophysics of N,Si-chelated complexes of Ir(III) and Rh(III) are quite distinct from the chemistry and photophysics of ortho-metalated 2-phenylpyridine Ir(III) and Rh(III) complexes. Standard synthetic routes to the latter utilize precursors containing the metals in the same formal oxidation state as is found in the products. While a combination of oxidative addition and reductive elimination processes may give rise to the ortho-metalated products, these products may also result from electrophilic substitution reactions. The routes to N,Si-chelated complexes described above begin with Rh(I) and Ir(I) precursors which are more likely to undergo oxidative addition reactions at one or more stages before reaching the final Rh(III) and Ir(III) products.

The distinct character of the absorption and emission spectrum of Ir(mesiqn)$_2$(CO)(Cl) (Fig 3) in comparison to the other four complexes described above (Fig 4 and 5) is attributed to the strong pi-acceptor nature normally associated with the CO ligand. The backbonding ability of CO is expected to move excited states corresponding to charge transfer from Ir(III) to the quinoline ring to high energies. The complete absence in $Ir(mesiqn)_2(CO)(Cl)$ of near uv/visible absorption features other than those attributed to the pi-pi^* transition of the quinoline system indicates this effect is large indeed. Prior studies of $Ir(ppy)_2(CO)Cl$ in comparison to $Ir(ppy)_3$ (4c) indicate a similar behavior in those species. Furthermore, the CO stretching frequency, which is often taken as a measure of the degree of backbonding, is found to be similar in $Ir(mesiqn)_2(CO)(Cl)$ and in $Ir(ppy)_2(CO)(Cl)$ (2003 cm^{-1} and 2015 cm^{-1}, respectively).

The spectral properties of <u>fac</u>-$M(mesiqn)_3$ and $M(mesiqn)_2Cl$ (Fig 4, 5) provide a basis for comparison to the related ortho-metalated fac-$Ir(ppy)_3$ and $[M(ppy)_2Cl]_2$ species. The structured emission of $Ir(ppy)_3$ in ethanol/methanol glass at 77 K has a sharp maximum at 495 nm (7) in comparison to the unstructured emissions of $Ir(mesiqn)_3$ and $Rh(mesiqn)_3$ which maximize in the region around 600 nm. Although 5-coordinate bis-ortho-metalated 2-phenylpyridine complexes of Rh(III) and Ir(III) are not known, the related dimers, $[M(ppy)_2Cl]_2$, have structured emissions in ethanol/methanol/dichloromethane glass at 77 K (15). These sharp maxima are found at about 490 nm (Ir) and 460 nm (Rh), substantially higher in energy than the $Ir(mesiqn)_2Cl$ and $Rh(mesiqn)_2Cl$ emissions.

The vast differences in the energies and structures of the four emission spectra in Figs 4 and 5 from the emission of $Ir(mesiqn)_2(CO)Cl)$ (Fig 3) indicate that a quinoline-localized excited state is not responsible for the emissions of $M(mesiqn)_3$ or $M(mesiqn)_2Cl$. The emission spectra are reminiscent of the metal-centered emissions seen in many Rh(III) ammine complexes (16, 17), but metal-centered states are expected to lie at much higher energies in these N,Si-chelated species due to the large d-orbital splittings anticipated for ligands such as mesiqn. This is confirmed by the observation of quinoline-localized emission in $Ir(mesiqn)_2(CO)Cl)$ as well as by the absence of any major effects on the position of the emission band maxima in going from $M(mesiqn)_2Cl$ to fac-$M(mesiqn)_3$ or from M = Rh(III) to M = Ir(III).

Application of the ligand field model, which emphasizes separability of metal and ligand orbitals, would suggest assignment of the emissions in Figs 4 and 5 to charge-transfer excited states, comparable to the MLCT assignments of the

$Ir(ppy)_3$ and $[Ir(ppy)_2Cl]_2$ emissions. However, several factors suggest that the MLCT assignment is inappropriate. For example, the emission lifetime of $Ir(mesiqn)_3$ at 77 K (28 us) is more than five times as long as that of $Ir(ppy)_3$ (5 us), even though the latter has been estimated (7) to be the radiative lifetime (emission yield of unity). Only of few cases of MLCT in Rh(III) complexes have been reported (18,19), and the lifetime of the $Rh(mesiqn)_3$ emission (300 us) is far longer than any representative lifetimes of MLCT excited states of other Rh(III), Ir(III) or Ru(II) complexes. In addition, the observation of emissions in $Rh(mesiqn)_3$ and in $Rh(mesiqn)_2Cl$ which are only slightly blue-shifted from the emissions of the analogous Ir(III) species is not anticipated in view of the difficulty generally associated with oxidation of Rh(III) relative to Ir(III). For example, the long-lived emission of $[Rh(ppy)_2Cl]_2$ from a pi-pi* excited state is supplanted by a lower energy, shorter-lived emission from an MLCT excited state in $[Ir(ppy)_2Cl]_2$ (15) due to the ease with which Ir(III) can be oxidized relative to Rh(III).

The approach taken here begins with recognition of the high degree of covalency which may occur in binding of Si to metal centers. In pseudo-octahedral d^6 complexes, sigma interaction of low-energy filled ligand donor orbitals with higher energy metal d-orbitals leads to filled sigma-bonding orbitals which are primarily ligand in character and empty sigma* antibonding orbitals which are largely based upon metal d-orbitals ($d_{x^2-y^2}$ and d_{z^2}). As the energy of the ligand donor orbitals is raised towards the energy of the metal d-orbitals, the metal-ligand sigma-bonding orbitals begin to have more metal d-orbital character and the empty sigma*-orbitals to have more ligand character. This mixing of ligand and metal character in the sigma and sigma* orbitals leads to the possibility for several types of transitions which are distinct from those based upon the simplier ionic model (Fig 6). These include excited states arising from the following types of transition: (M-Si) sigma - (M-Si) sigma*; (M) d-pi - (M-Si) sigma*; and (M-Si) sigma - (L) pi* CT. These types have been studied with absorption and emission spectroscopy in binuclear metal carbonyl complexes (20) such as $Re_2(CO)_8(phen)$ (21) and, more recently, in the photochemistry of $Mn_2(CO)_8(diimine)$ (22).

Even more relevant to the present work are studies of the emission and absorption spectroscopy and photochemistry of complexes using ligands such as (Ph_3Sn) and (Ph_3Ge) (23,24). Binding of Ge or Sn to a d^6 metal center should be represent-

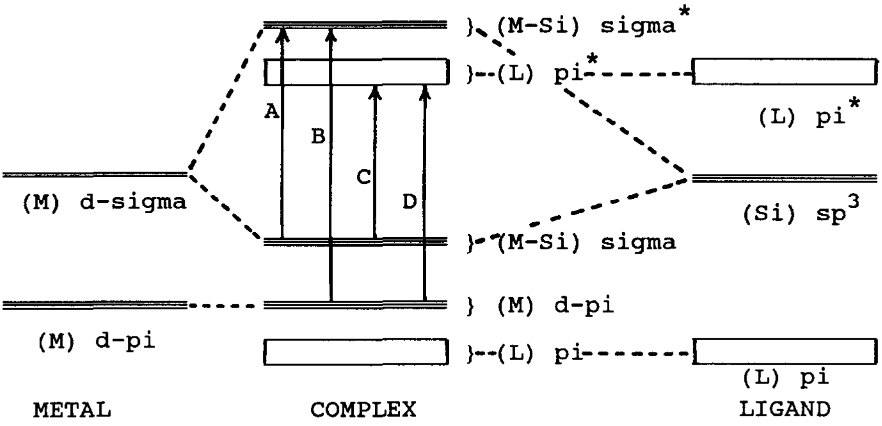


Figure 6. Schematic Representation of Orbital Transitions of Mesiqn Complexes of Rh(III) and Ir(III).
A) (M-Si) sigma - (M-Si) sigma*; B) (M) d-pi - (M-Si) sigma*; C) (M-Si) sigma - (L) pi* CT; D) (M) d-pi - (L) pi* CT

ative of a further extension of the trend in going from M-C bonding to M-Si bonding. Examples of M-Sn and M-Ge bonded species which have been studied include Ph$_3$SnRe(CO)$_3$(phen) and Ph$_3$GeRe(CO)$_3$(phen). These complexes are strongly emissive in EPA glasses at 77 K, with broad emission maxima at 635 nm and 660 nm, respectively. Lifetimes of 120 us and 110 us, respectively, have been reported (23b), and these emissions have been assigned to (Re-Sn) sigma - (phen) pi* CT or (Re-Ge) sigma - (phen) pi* CT.

This prior work on Re-Sn and Re-Ge bonded species provides some support for assignment of the emissions in Figs 4 and 5 to excited states of the type (Ir-Si) sigma - (quin) pi* CT and (Rh-Si) sigma - (quin) pi* CT. However, the intermediate position of M-Si bonding between M-C bonding, where covalency seems to have little effect on assignment of excited states of ortho-metalated species, and M-Sn or M-Ge bonding, where covalency is of great importance in assignment of excited states, may give rise to some mixing of states appropriate to each limit. In particular, close proximity of MLCT and (M-Si) sigma - (L) pi* CT states might be important with metal centers such as Ir(III), where the metal is relatively easy to oxidize due to the presence of relatively high energy filled metal d-pi (d_{xy}, d_{xz}, d_{yz}) orbitals. This possibilty, as well as the possibility of other excited states such as (M-Si) sigma - (M-Si) sigma* and (M) d-pi - (M-Si) sigma* cannot be eliminated from consideration in assignments of the absorption and emission of the mesiqn complexes of Ir(III) and Rh(III) at this time.

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