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Photophysics and Photochemistry of Rhenium(V)-Nitrogen Triple Bonds

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Abstract

Photophysical and photochemical studies on new nitrido and imido complexes of the type $[NRe(diphos)_2Cl]^+$ and $[PhNRe(diphos)_2Cl]^{2+}$ respectively, enable a direct comparison of excited state properties to be made (diphos is a diphosphine ligand). The two main findings follow are; 1) that the excited states are dramatically more nucleophilic than the ground state, and, 2) that the "ligand field" of the phenylimido group is weaker than that of the nitrido ligand.

1. Introduction

The synthesis and reactivity of transition metal-main group element multiple bonds have been subjects of numerous studies [1]. Seriously underrepresented, however, are studies of their photophysics and photochemistry. The importance of the photochemistry of metal-element multiple bonds can be found in their application to small molecule cleavage and reactivity, for example, that shown in Figure 1.

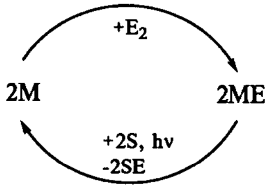


Figure 1. Hypothetical cycle for the metal-catalyzed reaction of a metal precursor (M) with a symmetrical small molecule (E_2) followed by photochemical reaction with a substrate (S).

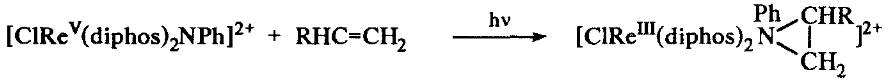
In the figure, a low-valent precursor (M) engages in activation and homolytic cleavage of a symmetrical small molecule (E_2), which as shown in Table 1 can be a variety of molecules from acetylenes to O_2. The ultimate product is the metal-element multiple bonded complex, ME. In a second, photochemical step ME reacts with a substrate (S) to regenerate M and form the high energy product SE.

Table 1. Products from the cleavage of a precursor (E_2) with the low-valent complex, M.

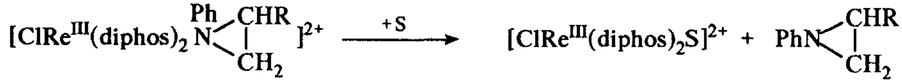
Precursor	**ME Product**	**Nomenclature**
alkene	$M(CR_1R_2)$	alkylidene
alkyne	MCR	alkylidyne
diazo-	MNR	imido
dinitrogen	MN	nitrido
dioxygen	MO	oxo

Such a cycle could be catalytic for the production of fuels or chemicals. A hypothetical example is that shown in Eqs. 1-3, where S is a labile solvent such as THF.

$$2[\mathrm{ClRe^{III}(diphos)_2S}]^{2+} + \mathrm{PhN{=}NPh} \longrightarrow 2[\mathrm{ClRe^{V}(diphos)_2NPh}]^{2+} \qquad (1)$$



$$[\mathrm{ClRe^{V}(diphos)_2NPh}]^{2+} + \mathrm{RHC{=}CH_2} \xrightarrow{h\nu} [\mathrm{ClRe^{III}(diphos)_2N(Ph)CHRCH_2}]^{2+} \qquad (2)$$



$$[\mathrm{ClRe^{III}(diphos)_2N(Ph)CHRCH_2}]^{2+} \xrightarrow{+S} [\mathrm{ClRe^{III}(diphos)_2S}]^{2+} + \mathrm{PhN(CHRCH_2)} \qquad (3)$$

Eq.1, where the diazo complex is cleaved by reaction with a Re^{III} complex, can be effected thermally, photochemically or electrochemically depending on the properties of the metal center. Eq. 2 depicts the formation of an excited imido complex which then reacts in a fast step with the alkene substrate. Finally, in Eq.3, the amine product is displaced by solvent (S) to complete the catalytic cycle.

2. Photochemistry and Photophysics of Transition Metal-Main Group Triple Bonds

In order to achieve light-driven cycles like those shown above a thorough understanding of the reactivity and physical properties of the excited state of transition metal-main-group multiple bonds must be attained. For the purpose of our work we have focused on those complexes which formally possess a bond order of three. From previous work, alkylidynes are the most studied, although predominantly form the point of view of preparative or descriptive photochemistry. Examples include photoprotonation to yield a coordinated alkylidene [2], coupling of an alkylidyne to a carbonyl ligand [3-6], attack of a free alkyne to give a coordinated cyclopropenyl ligand [7], transformation to a π-allyl ligand [8] and photo-oxidation with retention of the metal-carbon triple bond [9]. It appears that all of these processes can be described as a consequence of two types of reactivity, either enhanced excited state nucleophilicity at carbon or excited state electron transfer coupled with ligand exchange. Only a limited number have been concerned with photophysical processes [9, 10].

A few photophysical studies of oxometal and nitridometal complexes have been presented: these set the ground rules for an understanding of their photochemistry. For example, in the d^2 species *trans*-$[O_2Re^{V}(py)_4]^+$ [11-13], *trans*-$[O_2Os^{VI}(cyclam)]^{2+}$ [14], *trans*-$[O_2Os^{VI}(CN)_4]^{2-}$ [14], $[NOs^{VI}Cl_4]^-$ [15,16], *trans-trans*-$[NOs^{VI}Cl_4(H_2O)]^-$ [15], and $[NOs^{VI}(NH_3)_4]^{3+}$ [17] the lowest absorbing and emitting excited states are based on a spectroscopic transition that is predominantly $(d_{xz}, d_{yz})^1(d_{xy})^1 \leftarrow (d_{xy})^2$ in nature (in C_{4v} symmetry) where the $(d_{xz}),(d_{yz})$ set is mixed to varying degrees with p_x and p_y on N to give the π bonding and antibonding symmetry components of the triple bond and d_{xy} is nonbonding with respect to the metal nitrogen axis. *Trans*-$[O_2Re^{V}(py)_4]^+$, *trans*-$[O_2Os^{VI}(cyclam)]^{2+}$, and $[NOs^{VI}(NH_3)_4]^{3+}$ all exhibit long-lived emission in fluid solution, thus providing the spectroscopic handle for kinetic investigations relating to their photochmistry and photophysics. So far, the characteristic excited state chemistry is that of redox quenching although in the case of $[NOs^{VI}(NH_3)_4]^{3+}$ reductive quenching with a sacrificial donor leads to N-N coupling with the formation of the dinitrogen bridged dimer $[(CH_3CN)(NH_3)_4]OsNNOs[(NH_3)_4(CH_3CN)]^{5+}$ [18].

3. Photophysics and Photochemistry of Nitridorhenium(V) Complexes

Recently, we have described a new series complexes of the type $[NRe(diphos)_2Cl]^+$ containing the $[ReN]^{2+}$ chromophore which exhibit fluid solution luminescense at room temperature [19]. The lowest energy absorption and emission features of the complexes can be described as originating from triplet components of states associated with the $(d_{xz}, d_{yz})^1(d_{xy})^1 \leftarrow (d_{xy})^2$ transition like those examples cited above. In order to more fully describe their photophysical properties we have extended our studies to aryl containing diphophines. Typical absorption, emission, lifetime and quantum yield data are shown in Table 2. The diphos abbreviations are, 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)ethylene (dppene), 1,2-bis(diphenylphosphino)benzene (dppb) and 1,2-bis(dicyclohexylphosphino)ethane (dcype).

Table 2. Excited state properties of the $[NRe(diphos)_2Cl]^+$ complexes in CH_3CN solution .

Diphos	**Absorption (nm)**	**Emission(nm)**	**ϕ_r**	**τ (ns)**
dmpe	364 (410sh)	504	0.0012	360
depe	365 (410sh)	508	0.0009	240
dppe	360	500	<10-5	---
dppene	360 (413sh)	505	<10-5	---
dcype	362	none	---	---

Emission quantum yields for the dmpe and depe complexes are ca. 10^{-3} in CH_3CN solution at room temperature while fall in the range of 200 to 400 ns. Of particular interest is the observation that the lifetimes and ϕ_r can be ranked in the order dmpe > depe > dppe ˜ dppene ˜ dcype. Although the factors responsible for excited state decay in the complexes are under study it is reasonable to assume (from the ϕ_p and τ data) that radiationless decay to the ground state is a dominant mechanism. Furthermore, the "accepting modes" which control intramolecular energy dissipation in the ground state appear to involve the ReN vibration (see Figure 3), but reasonably involve other modes as well. Experimentally, the latter seems to be demonstrated in that the complexes with the greatest number of total molecular vibrations have the shortest lifetimes.

Returning to consideration of the electronic structure of the excited state, mixing of p_x and p_y orbitals on N with d_{xz} and d_{yz} orbitals on Re produces π interactions in the ground state and π^* interactions for the excited state. Thus, the thermally equilibrated excited state should have a reduced bond order and enhanced electron density at nitrogen relative to the ground state. In accord with this electronic description excited state protonation can be observed under conditions where the ground state is unprotonated. For $[NRe(dmpe)_2Cl]^+$ this is manifested as increased luminescence quenching as pH is lowered (Figure 2). This is expressed in reaction 4.

$$[NRe(dmpe)_2Cl]^{+,*} + H^+ \rightarrow [HNRe(dmpe)_2Cl]^{2+,*} \tag{4}$$

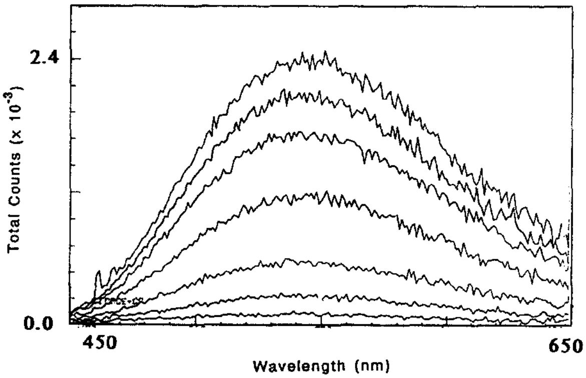


Figure 2. Quenching of the emission of $[NRe(dmpe)_2Cl]^+$ in aqueous solution as the pH is decreased. Proceeding from top to bottom the pH is 5.7, 5.1, 4.6, 4.2, 3.7, 3.2, and 2.7

The imido complex formed does not exhibit luminescence in the visible region. In the future we hope to exploit this photochemical pathway in order to effect nucleophilic attack of nitridorhenium complexes at various inorganic and organic electrophiles.

4. Emitting Imidos

Although the parent complex $[HNRe(dmpe)_2Cl]^{2+}$ is non-emissive the phenylimido analog $[PhNRe(dppe)_2Cl]^{2+}$ is very weakly emissive in CH_3CN solution at room temperature. We have prepared a family of new phenylimido complexes by a simple, two-step procedure as shown in Eqs. 5 and 6.

$$ORe(PPh_3)_2Cl_3 + PhNH_2 \rightarrow PhNRe(PPh_3)_2Cl_3 + H_2O \tag{5}$$

$$\mathrm{PhNRe(PPh_3)_2Cl_3 + 2diphos \rightarrow PhNRe(diphos)_2Cl^{2+} + 2PPh_3 + 2Cl^-} \qquad (6)$$

In a Eq. 5 diphos can be a variety of ligands including dppe and dppene. For dppb, however, the reaction unexpectedly give the hydoxo complex $PhNRe(diphos)_2OH^{2+}$. The complexes have been characterized by UV-visible, infrared, and NMR spectroscopies, and by elemental analysis.

All the complexes exhibit a low energy absorption manifold of weak absorptivity in the region 550 to 542 nm, for which a corresponding emission maxima are found at ca. 750 nm. To our knowledge these are the first examples of luminescence from imido complexes. Lifetimes of the complexes have yet to be determined but ϕ_r is in the range of 10^{-5} to 10^{-4}. By analogy to spectral assignments for $[NRe(dmpe)_2Cl]^+$ and its analogs the lowest energy absorption and emission processes can be assigned as spectrocopic transitions that are predominantly $(d_{xz}, d_{yz})^1(d_{xy})^1 \leftarrow (d_{xy})^2$ in nature. Given this assignment, an instructive comparison can be made of the emission spectra of the isoelectronic and isostructural complexes $[NRe(dppe)_2Cl]^+$ and $[PhNRe(dppe)_2Cl]^{2+}$ at 77° K in 4:1:1 EtOH/MeOH/DMF glass (Figure 3).

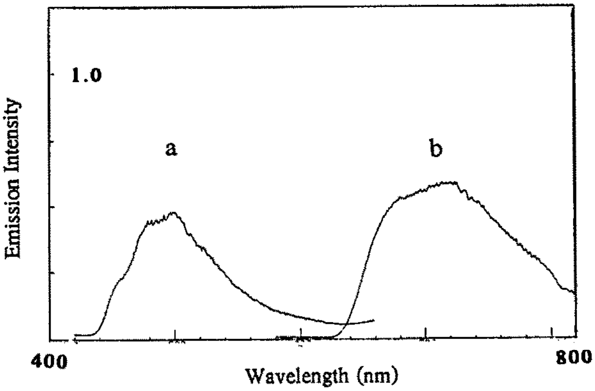


Figure 3. Emission spectra (different scales) of a) $[NRe(dppe)_2Cl]^+$ and b) $[PhNRe(dppe)_2Cl]^{2+}$ in a 4:1:1 EtOH/MeOH/DMF glass at 77° K.

Of note is the appearance of vibrational structure of ca. 1050 cm^{-1} for both triple bonded complexes and the exceedingly large energy difference between the vibronic origins (ca. 6700 cm^{-1}). This latter observation is most likely a consequence of the stabilization of the (d_{xz},d_{yz}) orbitals. This is supported by the cyclic voltammetry of both complexes in CH_3CN solution at room temperature (0.1 M TBAH as supporting electrolyte; vs. SCE) which shows reduction processes at -0.6V for $[PhNRe(dppe)_2Cl]^{2+}$ and -1.7V for $[NRe(dppe)_2Cl]^+$.

5. Conclusions

Specific preparative chemistry has allowed us to compare, in a preliminary fashion, the excited state properties of nitrido and imido complexes in the same, or very similar coordination environments. A combination of spectroscopic and electrochemical data leads to the conclusion that the HOMO-LUMO gap in the phenylimido complexes is much smaller than in the analogous nitride. This can be explained by less $d\pi(Re)/p\pi(N)$ mixing in the former leading to a stabilization of the π^* orbitals.

For $NRe(dmpe)_2Cl^+$ a general increase in nucleophilicity is observed upon excitation, as evidenced by the protonation of the excited state at the nitrido nitrogen. A likely predicition is that this photochemical pathway will also be observed for imido complexes, but of reduced magnitude due to reduced N p character in the excited state. Our future studies will address this issue as well as concentrating on the synthesis, photochemistry and photophysics of isostructural oxo- and alkylidyne analogs.

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