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Short Communication

Metal to ligand charge transfer photochemistry of Re(I)–alkyl complexes

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Abstract

A preliminary study has been carried out concerning the photochemistry and photophysics of a series of $(bpy)Re^I(CO)_3$–R complexes, where bpy is 2,2′-bipyridine and R = –CH_3, –CH_2Ph and –Ph. Photolysis of the complexes into the lowest energy absorption band (436 nm) leads to a highly efficient Re–C bond homolysis reaction for R = –CH_3 and –CH_2Ph. Absorption and low-temperature emission studies of the complexes suggest that the lowest excited state is based on $d\pi$ (Re) → π^* (bpy) metal to ligand charge transfer (MLCT). Nanosecond transient absorption studies confirm that the MLCT state is formed after near-UV excitation of $(bpy)Re(CO)_3$–Ph; however, only the reactive intermediate which is formed as a result of Re–C bond homolysis is observed for $(bpy)Re(CO)_3$–CH_3 and $(bpy)Re(CO)_3$–CH_2Ph. The results are interpreted by a photochemical model in which the bond homolysis reaction occurs either directly from an unrelaxed MLCT excited state or from a spectroscopically silent state which is reached during non-radiative relaxation of the Franck-Condon MLCT state.

Introduction

Bimetallic complexes of the type, $(diimine)Re^I(CO)_3$–M where M is a metal fragment such as $Mn(CO)_5$, $Re(CO)_5$ or SnR_3, undergo efficient unimolecular photochemical decomposition via Re–M bond homolysis [1–3]. Although the outcome of this photoreaction is clear, the reactive excited state has not been assigned. Spectroscopic and electrochemical studies suggest that the energies of the bonding metal–metal orbital, σ_{Re-M}, and the Re-based $d\pi$ orbitals are comparable [2]. As a result, two charge-transfer configurations are possible candidates for the lowest excited state of the Re–M complexes: one based on $d\pi$ (Re) → π^* (diimine) metal-to-ligand charge transfer (MLCT), and another based on $\sigma_{Re-M} \rightarrow \pi^*$ (diimine) charge transfer (σ,π^* CT). In addition to these CT transitions, a state based on $\sigma_{Re-M} \rightarrow \sigma^*$ is anticipated to be accessible at higher excitation energy [3].

We recently began photochemical and photophysical studies of a series of *fac*-$(bpy)Re^I(CO)_3$–R complexes, where R is alkyl or aryl and bpy is 2,2′-bipyridine. (These complexes are collectively abbreviated as Re–R. Specific abbreviations are: R = –CH_3, Re–Me; R = –CH_2Ph, Re–Bz; R = Ph, Re–Ph). Photolysis of the Re–R complexes with visible or near-UV light leads to highly efficient Re–C bond homolysis, in direct analogy to the photochemical reactivity which has been observed for $(diimine)Re^I(CO)_3$–M complexes. Spectroscopic experiments on the Re–R complexes indicate that the lowest excited state is the $d\pi$ (Re) → π^* (bpy) MLCT and, as a result, these complexes provide examples of *reactive* systems in which MLCT is clearly the lowest excited state. The reactivity of the Re–R complexes is best explained by a photochemical mechanism which involves prompt bond homolysis from an unrelaxed MLCT state or from a spectroscopically silent dissociative state which is populated efficiently via internal conversion from the Franck-Condon MLCT state.

Experimental

The compounds Re–Me, Re–Bz and Re–Ph were prepared by reaction of $(bpy)Re(CO)_3Cl$ with the appropriate Grignard reagent, R–MgCl, in THF solution [4]. The photochemical and photophysical experiments were carried out by using techniques and instrumentation that have been described in previous publications [5–7].

Results and discussion

Steady-state photochemistry

Visible (436 nm) or near-UV (366 nm) irradiation of either Re–Me or Re–Bz in solution leads to efficient photodegradation of the complex and appearance of products which are consistent with Re–C bond homolysis being the primary photochemical process. Photolysis of either complex in $CHCl_3$/0.1 M CCl_4 leads to formation of $(bpy)Re(CO)_3Cl$ (Re–Cl) as the predominant metal containing product. This product is consistent with the

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following reaction sequence:

$$(\mathrm{bpy})\mathrm{Re^I(CO)_3{-}R} \xrightarrow{h\nu} (\mathrm{bpy}^{\bullet -})\mathrm{Re^I(CO)_3} + \mathrm{R}^{\bullet} \xrightarrow{\mathrm{CCl_4}} (\mathrm{bpy})\mathrm{Re^I(CO)_3Cl} + \mathrm{R}^{\bullet} \quad (1)$$

where $(\mathrm{bpy}^{\bullet -})\mathrm{Re^I(CO)_3}$ is likely a 16-electron complex with a coordinated bpy anion radical [8]. No other Re-containing products were detected by chromatographic analysis (HPLC and TLC); however, a product in addition to Re–Cl was isolated from semi-preparative scale photolysis. This material is a yellow powder which is insoluble in all solvents tried. We tentatively identify this intractable material as the Re–Re dimer which would result from dimerization of $(\mathrm{bpy}^{\bullet -})\mathrm{Re^I(CO)_3}$. That alkyl radicals are formed during photolysis is supported by the observation of toluene as a major photoproduct of Re–Bz in CH_3OH solution.

Table 1 lists the results of quantum yield studies of the reaction of Re–Me, Re–Bz and Re–Ph in $CHCl_3$/0.1 M CCl_4 solution. Re–Me and Re–Bz photoreact with approximately unit quantum efficiency; however, the efficiency for the appearance of Re–Cl is lower. The fact that Re–Cl is not formed stoichiometrically could be due to formation of the dimeric product which is not observed under the HPLC analysis conditions. Interestingly, the aryl complex, Re–Ph is stable under 436 and 366 nm irradiation ($\Phi_- < 0.001$).

TABLE 1. Photochemical quantum yield data[a]

Complex	Φ_-(Re–R)[b]	Φ(Re–Cl)[c]
Re–Me	1.0 ± 0.2	0.3 ± 0.06
Re–Bz	0.9 ± 0.1	0.15 ± 0.05

[a]Studies in argon degassed $CHCl_3$/0.1 M CCl_4. [b]Quantum yield for disappearance of Re–R complex. [c]Quantum yield for formation of Re–Cl.

Photophysical observations

Figure 1 shows a comparison of the UV–Vis absorption spectra of Re–Cl and Re–Me; the spectra of Re–Bz and Re–Ph are qualitatively similar. It is clear that there is excellent qualitative agreement between the spectra of Re–Me and Re–Cl. The lowest energy absorption for Re–Cl has been previously assigned to arise mainly from $d\pi$ (Re)$\rightarrow\pi^*$ (bpy) MLCT [9]; the similarity in the position and bandshape of the lowest energy transition for Re–Me strongly suggests that this band is an MLCT transition as well. The red-shift in the position of the MLCT absorption of Re–Me compared to Re–Cl is consistent with the stronger σ-donor capacity of the alkyl ligand compared to Cl [10].

Luminescence experiments were conducted on Re–Me and Re–Ph at temperatures ranging from 77 to 140 K in an EtOH/MeOH (4:1 vol.:vol.) solvent glass. At 77 K a broad, structureless emission is observed from both complexes (Re–Ph, $\lambda_{max} = 632$ nm; Re–Me, $\lambda_{max} = 684$ nm). As the temperature is raised from 77 to 140 K, the emission maximum of both complexes red-shifts and the intensity decreases sharply. At 140 K the intensity is less than 5% of that observed at 77 K, and at 298 K no emission is detectable. The emission decays of both complexes at 77 K follow multiexponential kinetics, but the mean lifetimes obtained from multiexponential fits are 7.8 and 2.3 μs for Re–Ph and Re–Me, respectively. The low-temperature ^{3}MLCT emission of Re–Cl has been reported and is quite similar to the emission which is observed from the Re–R complexes (Re–Cl in EPA, $\lambda_{max} = 530$, $\tau_{em} = 3.8$ μs) [11]. The similarity of the emission bandshapes and lifetimes for the two Re–R complexes compared to Re–Cl strongly suggests that the origin of the low-temperature emission from the Re–R complexes is the ^{3}MLCT state.

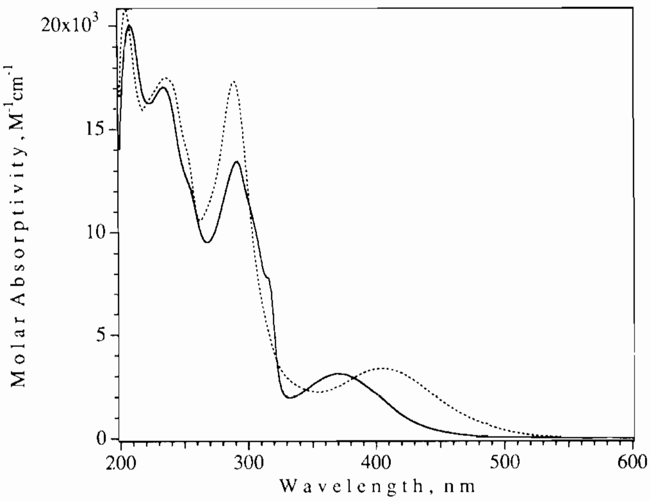

Fig. 1. UV–Vis absorption spectra in CH_3CN solution: – – –, (bpy)Re(CO)$_3$–CH$_3$; ——, (bpy)Re(CO)$_3$–Cl.

Nanosecond laser flash photolysis experiments were carried out on Re–Cl, Re–Ph, Re–Me and Re–Bz in solution at 298 K to identify excited states and possible reactive intermediates that are involved in the photochemistry and photophysics of these complexes. Figure 2(a) shows the transient absorption (TA) spectrum observed for Re–Cl in CH_3CN solution at 0 ns delay time. This spectrum is assigned to the MLCT state based on its similarity to the absorption of MLCT states of related d^6 metal complexes [12, 13]. In accord with this assignment, the transient absorption of Re–Cl decays with $\tau = 25$ ns, in good agreement with the MLCT emission lifetime (33 ns). Figure 2(b) shows the TA spectrum of Re–Ph in CH_3CN at 0 ns delay after excitation; the similarity between this spectrum and that for Re–Cl indicates that the transient which is produced by near UV excitation of Re–Ph is the MLCT excited state.

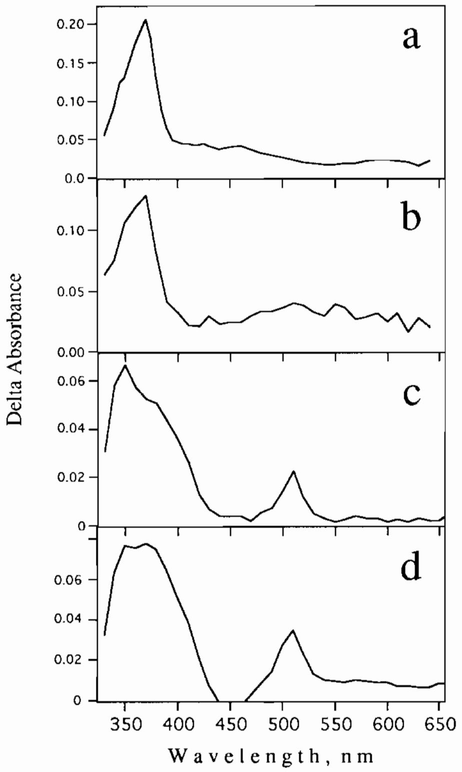

Fig. 2. Transient absorption spectra at various delay times following a 355 nm excitation pulse (6 ns fwhm, 10 mj/pulse). (a) (bpy)Re(CO)$_3$Cl in CH$_3$CN solution, 0 ns delay. (b) Re–Ph in CH$_3$CN solution, 0 ns delay. (c) Re–Bz in toluene, 13 μs delay. (d) Re–Me in toluene, 13 μs delay.

The TA difference spectra for Re–Me and Re–Bz differ considerably, both in bandshape and temporal behavior, compared to the typical MLCT difference spectra observed for Re–Cl and Re–Ph. Figure 2(c) and (d) shows the spectra of Re–Bz and Re–Me in toluene at 13 μs delay following excitation. The 13 μs delay spectra are identical to those observed immediately following the laser pulse; in both cases the transient which is responsible for the spectrum does not decay appreciably at delay times to 20 μs. The transient which gives rise to the spectrum observed for Re–Bz and Re–Me is attributed to the radical, (bpy$^{\cdot-}$)Re^{I}(CO)$_3$, a 16-electron complex with a coordinated bpy anion radical, which is formed in the bond fragmentation reaction [8]. The strong absorption in the near-UV region is likely due to π^*,π^* transitions of the bpy anion radical [13]. It is important to note that for both complexes the transient spectrum attributed to the radical appears promptly during the laser pulse, indicating that Re–C bond fragmentation in Re–Bz occurs with $k \geqslant 10^9$ s^{-1}.

Conclusions

The photochemical studies indicate that photoexcitation of Re–Me or Re–Bz into the lowest absorption band leads to efficient metal–carbon bond homolysis, and the absorption and luminescence data imply that the lowest excited state of these complexes is based on $d\pi$ (Re)$\rightarrow \pi^*$ (bpy) MLCT. However, nanosecond transient absorption does not provide evidence for the involvement of the MLCT state in the Re–C bond homolysis: the reactive intermediate, (bpy$^{\cdot-}$)Re^{I}(CO)$_3$, is formed promptly during the ns laser pulse. Based on this result, we infer that Re–C homolysis is exceedingly rapid ($k \geqslant 10^9$ s^{-1}); therefore, sufficient time is not available for fragmentation to be a thermally activated process which occurs from a relaxed ^{3}MLCT state.

In order for Re–C bond fragmentation to occur, it is likely that energy in excess of the Re–C bond energy ($D_{\text{Re–C}}$) must be provided by photoexcitation. Although $D_{\text{Re–C}}$ values for the Re–R complexes are not available, a limited number of M–C bond energies are available for some related carbonyl complexes [14]. From this data the following estimates for $D_{\text{Re–C}}$ can be made: Re–Ph ($D_{\text{Re–C}} \approx 57$ kcal), Re–Me ($D_{\text{Re–C}} \approx 53$ kcal) and Re–Bz ($D_{\text{Re–C}} \approx 40$ kcal). The low temperature emission studies of Re–Me and Re–Ph indicate that the energy of the relaxed ^{3}MLCT state is $E(^3\text{MLCT}) = 44 \pm 3$ kcal. The estimates for $D_{\text{Re–C}}$ coupled with the value for $E(^3\text{MLCT})$ suggest that insufficient energy is available for bond homolysis to occur from a *relaxed* ^{3}MLCT state. However, despite this fact, the results indicate that photoinduced bond homolysis occurs rapidly. Given the fact that photon absorption apparently produces the Franck-Condon ^{1}MLCT state, bond homolysis must occur either via fast non-radiative decay of the ^{1}MLCT state into a vibrationally hot ground state, or via internal conversion into a dissociative state which is not clearly apparent in the absorption spectra [3, 15]. Although the nature of the possible dissociative excited state is uncertain, preliminary INDO calculations [16] indicate that: (i) all of the states within 5 kK of the lowest transition have MLCT character; (ii) other than MLCT, only states having σ,π^* CT character are within 10 kK of the lowest transition [17].

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