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## Direct Observation of Ultrafast C–C Bond Fragmentation in a Diamine Radical Cation

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Nanosecond and picosecond transient absorption studies were carried out on *fac*-(bpy)Re<sup>I</sup>(CO)<sub>3</sub>(DA)<sup>+</sup> (**1**), where bpy is 2,2'-bipyridine and DA is the 1,2-diamine-substituted pyridine *erythro*-1-[*p*-[4-(pyridyl)methyl]anilino]-2-piperidino-1,2-diphenylethane. Photoexcitation of the  $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$  metal-to-ligand charge-transfer excited state in **1** initiates the following sequence: (1) forward electron transfer from the 1,2-diamine unit to the photoexcited (bpy)Re(CO)<sub>3</sub><sup>+</sup> chromophore to produce the ligand-to-ligand charge transfer (LLCT) state, (bpy<sup>•-</sup>)Re<sup>I</sup>(CO)<sub>3</sub>(DA<sup>•+</sup>); (2) C–C bond fragmentation of the diamine radical cation unit. Nanosecond transient absorption spectral data indicate that the  $\alpha$ -amino radical which is the primary product of the C–C bond fragmentation is produced during the 10 ns laser excitation pulse. Picosecond pump–probe studies of **1** allow direct determination of the kinetics of back electron transfer in the LLCT state ( $1 \times 10^8 \text{ s}^{-1}$ ) and for C–C bond fragmentation in the diamine radical cation ( $3 \times 10^8 \text{ s}^{-1}$ ).

## Introduction

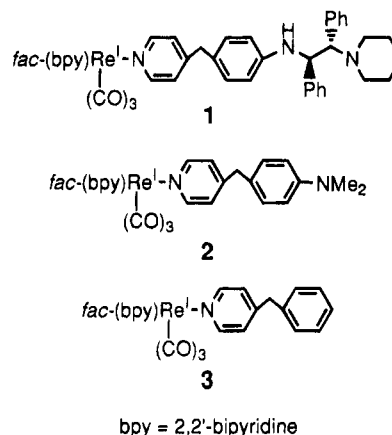
Radical ions are often produced by photoinduced electron transfer, and in many instances they undergo rapid irreversible chemical reactions such as isomerization, rearrangement, bond fragmentation, or deprotonation.<sup>1–10</sup> Recently, it has been demonstrated that the irreversible reactions of photoproduct radical ions can be used to probe the mechanism and dynamics of both inter- and intramolecular photoinduced electron transfer reactions.<sup>2,4–7,11,12</sup>

We have been investigating the mechanism and dynamics of carbon–carbon bond fragmentation reactions in  $\alpha$ -amino alcohol and 1,2-diamine radical cations that are produced by inter- and intramolecular photoinduced electron transfer.<sup>11–14</sup> Our work is motivated by an interest in applying the C–C bond fragmentation reaction as a “clock” to probe the dynamics of back electron transfer in charge-separated intermediates that are produced by electron transfer quenching. Prior to application of the C–C bond fragmentation probe for the dynamics of back electron transfer, however, it is necessary to “calibrate” the radical ion clock by determining the absolute rate of bond fragmentation.<sup>15,16</sup> The present communication reports the results of a study in which the rate of an ultrafast C–C bond fragmentation of a 1,2-diamine radical cation has been determined directly by picosecond transient absorption spectroscopy. This study demonstrates that bond fragmentation of the diamine radical cation is sufficiently rapid such that it competes effectively even with rapid back electron transfer in an intramolecular charge separated state. This study suggests that the diamine system may provide the basis for a series of radical ion probes that will be useful for “clocking” the dynamics of intramolecular charge transfer processes.

## Experimental Section

**Synthesis and Characterization.** The 1,2-diamine ligand *erythro*-1-[*p*-[4-(pyridyl)methyl]anilino]-2-piperidino-1,2-diphenylethane (**4**) was prepared by a route that was patterned after

## CHART 1



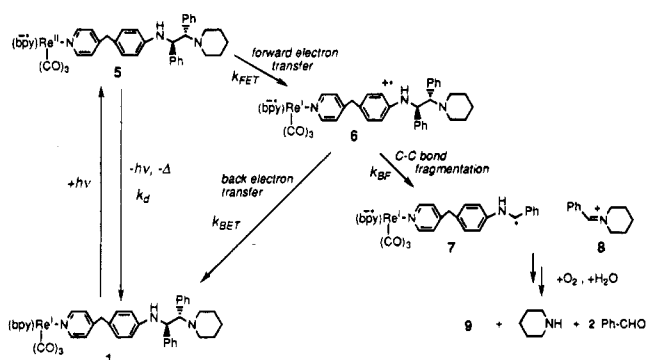
a literature method.<sup>11,17,18</sup> The diamine-substituted metal complex **1** (Chart 1) was prepared by reaction of **4** with (bpy)-Re<sup>I</sup>(CO)<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>), according to a method that has been previously described.<sup>11</sup> Complete details concerning the synthesis of **1** and **4** will be reported in a forthcoming paper,<sup>19</sup> and the synthesis and characterization of metal complexes **2** and **3** have been previously reported.<sup>13</sup>

**Spectral Data for 1.** <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$  1.28 (br, 2H), 1.36 (br, 4H), 2.15 (br, 2H), 2.43 (br, 2H), 3.62 (d,  $J$  = 8.1 Hz, 1H), 3.67 (s, 2H), 4.8–4.9 (m, 2H, NH), 6.38 (d,  $J$  = 8.1 Hz, 2H), 6.72 (d,  $J$  = 8.1 Hz, 2H), 7.02 (d,  $J$  = 6.3 Hz, 2H), 7.1–7.3 (m, 10H), 7.75 (t,  $J$  = 5.1 Hz, 2H), 8.02 (d,  $J$  = 6.3 Hz, 2H), 8.24 (t,  $J$  = 8.1 Hz, 2H), 8.36 (d,  $J$  = 8.1 Hz, 2H), 9.16 (d,  $J$  = 5.1 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN)  $\delta$  24.1, 25.8, 39.1, 51.1, 57.4, 74.8, 124.4, 125.8, 126.2 (2C's), 126.7, 127.1, 127.2, 127.4, 128.5, 128.9, 129.2, 136.8, 140.8, 142.6, 146.5, 151.2, 153.5, 155.5, 156.0. HRMS (FAB, positive ion) calcd for C<sub>44</sub>H<sub>41</sub>N<sub>5</sub>O<sub>3</sub>Re, 874.277 (M<sup>+</sup>); obsd, 874.273.

**Nanosecond and Picosecond Transient Absorption Spectroscopy.** All studies were carried out using argon degassed CH<sub>3</sub>CN solutions. Nanosecond transient absorption spectra and kinetics were obtained at the University of Florida on a system that has been previously described.<sup>20</sup> Samples were excited with the third harmonic output of a Q-switched Nd:YAG laser (355

<sup>†</sup> University of Florida.<sup>‡</sup> Georgia State University.<sup>®</sup> Abstract published in *Advance ACS Abstracts*, July 15, 1995.

## SCHEME 1

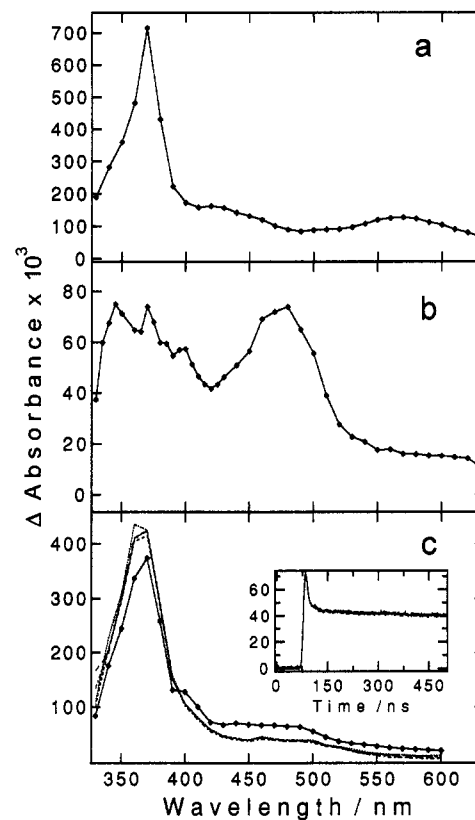


nm, 10 ns fwhm, 10 mJ/pulse dose). Kinetic traces obtained at each wavelength represent averages of 10 laser shots. Delay times for nanosecond transient absorption spectra refer to the delay time from the leading edge of the laser excitation pulse. Argon degassed samples were contained in a recirculating cell which contained 100 mL total sample volume in order to minimize sample decomposition during data acquisition. Sample concentration was adjusted to obtain an optical density of 0.5 at 355 nm (path length 1 cm,  $c \approx 1 \times 10^{-4}$  M).

Picosecond pump-probe experiments were carried out at Georgia State University on an instrument that has been previously described.<sup>21</sup> Samples were excited at a 15 Hz repetition rate with the third harmonic output of an active/passive mode-locked Nd:YAG laser (355 nm, 30 ps fwhm,  $\approx 6$  mJ/cm<sup>2</sup> per pulse). The following protocol was used in all picosecond experiments. A 250-mL volume of sample solution was thoroughly degassed by argon bubbling for 30 min. Sample concentrations were adjusted to attain an optical density at 355 nm of 0.25 or 0.5 for experiments carried out probe wavelengths set to 370 or 450 nm, respectively. After degassing, the sample container was connected to a magnetically coupled vane-pump which flowed the sample solution smoothly and rapidly through the 1-cm path length sample cell. The degassed liquid sample solution was continuously recirculated through the sample cell while pump-probe data were obtained at a fixed probe wavelength but at six different probe delay times. The six delay times were purposely selected to be random (the probe delay times were not sequential). Each of the six pump-probe data points obtained with the solution represents an average of 480 laser shots. After completion of six pump-probe data acquisition cycles, the sample solution was discarded and replaced with a freshly degassed 250-mL volume sample solution and the data acquisition cycle was repeated. Each of the three pump-probe kinetic traces shown in Figure 2 were constructed by combining data points from six to eight separate 250-mL sample solution batches.

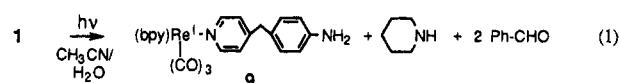
## Results and Discussion

Photochemical and photophysical studies of **1** and related "reactive donor ligand" substituted Re(I) complexes indicate that photoexcitation into the  $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$  metal to ligand charge transfer (MLCT) excited state of the  $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3$ -chromophore initiates a sequence which involves diamine donor to Re forward electron transfer followed by C-C bond fragmentation of the resulting diamine radical cation (Scheme 1).<sup>11-14</sup> First, evidence that forward electron transfer occurs is provided by the observation that the MLCT emission of **1** ( $\Phi_{\text{em}} \leq 10^{-4}$  and  $\tau_{\text{em}} \leq 0.5$  ns) and **2** ( $\Phi_{\text{em}} \leq 10^{-4}$  and  $\tau_{\text{em}} \leq 0.5$  ns) is strongly quenched relative to the MLCT emission of model complex **3** ( $\Phi_{\text{em}} = 0.045$  and  $\tau_{\text{em}} = 209$  ns) which does not contain the aniline electron donor.<sup>22</sup> Second, steady-state photochemical studies of **1** in air-saturated solution indicate that irradiation into the MLCT absorption induces a highly efficient



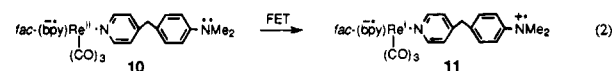
**Figure 1.** Nanosecond transient absorption difference spectra. All samples were excited at 355 nm (10 mJ/pulse, 10 ns fwhm) and the concentration of the metal complexes was  $1.2 \times 10^{-4}$  M in degassed  $\text{CH}_3\text{CN}$ . (a) **3** at 20 ns delay; (b) **2** at 10 ns delay; (c) **1** at 5 ns ( $\blacklozenge$ ), 100 ns (---), 200 ns (—), and 1000 ns ( $\cdots$ ) delay. Inset illustrates kinetics at 480 nm.

photochemical reaction ( $\Phi_{\text{rxn}} = 0.54$ ) that produces products with structures that are consistent with C-C bond fragmentation as the predominant excited state decay pathway, eq 1.<sup>11,19</sup>



A series of nanosecond and picosecond transient absorption studies were carried out to identify the reactive intermediates involved in the photochemistry of **1** and to determine all of the pertinent rate constants, including the rate of bond fragmentation of the diamine ligand-based radical cation. Figure 1 illustrates a series of nanosecond transient absorption spectra obtained on 1–3 using 355 nm excitation, which exclusively excites the MLCT absorption of the  $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3$ -chromophore. Figure 1a illustrates the spectrum of **3** at 20 ns delay. This spectrum, which is assigned to the  $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$  MLCT excited state, is dominated by a strong, narrow absorption band with  $\lambda_{\text{max}} = 370$  nm and  $\Delta A_{\text{max}} = 0.72$ . In accord with the MLCT assignment the transient decays with  $\tau = 210$  ns in degassed solution, in excellent agreement with the MLCT emission lifetime of the complex.

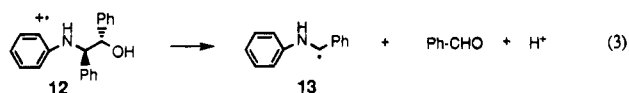
Figure 1b illustrates the transient absorption spectrum of **2** at 10 ns delay; this spectrum is dominated by a comparatively weak, broad absorption band with  $\lambda_{\text{max}} = 490$  nm and  $\Delta A_{\text{max}} = 0.078$ . This mid-visible absorption is assigned to the aniline radical cation that is present in the ligand to ligand charge transfer state (**11**) that is formed by forward electron transfer quenching of the MLCT state (**10**), eq 2.<sup>23</sup>



Although charge transfer state **11** was easily detected by nanosecond transient absorption, this species decays very rapidly on the nanosecond time scale, and therefore its lifetime was determined by monitoring the decay of the transient absorption signal at 480 nm by picosecond transient absorption spectroscopy (Figure 2a). Analysis of the picosecond data indicates that the lifetime of **11** is 9.6 ns, which indicates that the rate of back electron transfer ( $k_{\text{BET}}$ , Scheme 1) is  $\approx 1.0 \times 10^8 \text{ s}^{-1}$ .<sup>24</sup>

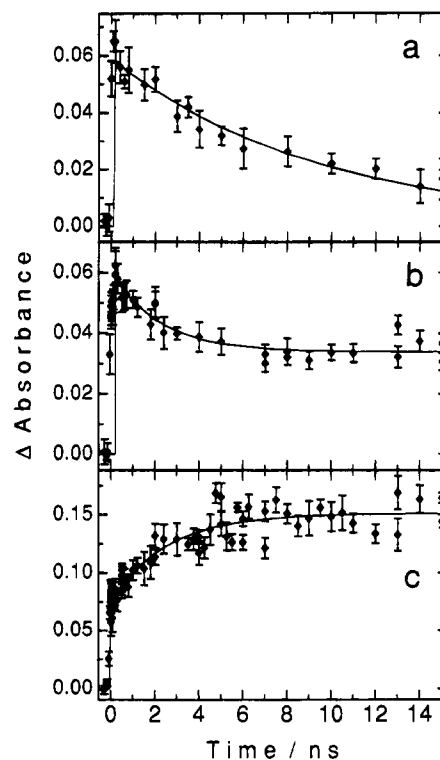
Figure 1c illustrates a series of nanosecond transient absorption spectra of diamine complex **1** in argon degassed solution acquired at delays of 5 (the peak of the laser pulse), 100, 200, and 1000 ns following the leading edge of the 10 ns excitation pulse. The initial spectrum (e.g., at 5 ns delay) displays slightly diminished  $\Delta A$  in the near-UV and slightly enhanced  $\Delta A$  in the mid-visible relative to the spectra observed at later delays. The initial rapid relaxation that occurs in the visible region is clearly evident from the inset to Figure 1c, which illustrates the temporal evolution of the  $\Delta A$  signal at 480 nm. The spectra observed at delay times ranging from 50 to 1000 ns are nearly superimposable and are characterized by a strong near-UV absorption with  $\lambda_{\text{max}} = 360 \text{ nm}$  and  $\Delta A_{\text{max}} = 0.43$ . Experiments carried out on longer time scales reveal that in argon-degassed solution this long-lived 360 nm transient decays with  $\tau \approx 300 \mu\text{s}$ ; however, in air-saturated solution the transient is rapidly quenched with  $\tau \approx 100 \text{ ns}$ .

Several lines of evidence support the premise that the 360 nm transient which is long-lived in degassed solution is the  $\alpha$ -amino radical complex **7** (Scheme 1). First, the transient absorption spectral changes that accompany C—C bond fragmentation of aniline radical cation **12** to  $\alpha$ -amino radical **13** have been examined by nanosecond flash photolysis; eq 3.<sup>14</sup>



Radical cation **12** absorbs moderately in the mid-visible (450–500 nm) while radical **13** absorbs strongly at  $\lambda_{\text{max}} = 360 \text{ nm}$  and weakly throughout the visible. It is significant that the absorption of **13** is very similar to the transient absorption of **1** at delay times greater than 50 ns following laser excitation. Both **13** and **7** possess the Ph—CH—NH—Ph chromophore, which is probably the origin of the 360 nm absorption. Second, previous work demonstrates that  $\alpha$ -amino radicals (e.g., **13** and related species) are quenched at nearly the diffusion-controlled rate by  $\text{O}_2$ , presumably by electron transfer from the radical to  $\text{O}_2$ .<sup>11</sup> The 360 nm transient observed following flash photolysis of **1** is quenched extremely rapidly in air-saturated solution, consistent with the expected reactivity if it is indeed an  $\alpha$ -amino radical. Finally, as noted above, in degassed solution, the 360 nm transient has a lifetime of  $\approx 300 \mu\text{s}$ , which is consistent with the premise that the transient is a free radical rather than an excited state.

The fact that the temporal evolution of the transient absorption spectrum of **1** is nearly complete during the nanosecond laser pulse suggests that **7** is formed by the following sequence: (1) photoexcitation to produce MLCT state **5**, (2) rapid forward electron transfer to produce charge separated state **6**, and (3) rapid C—C bond fragmentation of the diamine radical cation in **6** to produce **7**. Although steps 2 and 3 appear to be rapid on the nanosecond time scale, careful comparison of the transient absorption spectra at 5 and 100 ns delays (Figure 1c) suggests that the dynamics of at least one of these two steps can be resolved by picosecond transient absorption. However, before discussing the picosecond data, it is important to note that the nanosecond data suggests that at very early times (e.g.,  $< 10$



**Figure 2.** Picosecond pump-probe data,  $\Delta$  absorbance vs. probe delay time. All samples were excited at 355 nm ( $6 \text{ mJ}/\text{cm}^2$  per pulse, 30 ps fwhm). Samples contained in degassed  $\text{CH}_3\text{CN}$  solvent. (a) **2** at 480 nm ( $[\text{2}] \approx 1.2 \times 10^{-4} \text{ M}$ ); (b) **1** at 460 nm ( $[\text{1}] \approx 1.2 \times 10^{-4} \text{ M}$ ); (c) **1** at 370 nm ( $[\text{1}] \approx 6.0 \times 10^{-5} \text{ M}$ ).

ns) there is a noticeable increase in  $\Delta A$  in the near-UV (350–390 nm) and a noticeable decrease in  $\Delta A$  in the mid-visible (410–500 nm). Since these spectral changes are anticipated to accompany C—C bond fragmentation (e.g., **6**  $\rightarrow$  **7**, Scheme 1), it seemed that it would be possible to resolve the dynamics of this process with picosecond spectroscopy.<sup>25</sup>

Picosecond pump-probe experiments were carried out on **1** to temporally resolve the fast transient absorption changes observed in the nanosecond experiments. Probe wavelengths of 370 (Figure 2c) and 460 nm (Figure 2b) were selected based on the early time nanosecond transient absorption data.<sup>26</sup> Over the time scale ranging from 0 to 5 ns following excitation,  $\Delta A$  decays at 460 nm while  $\Delta A$  increases at 370 nm. These  $\Delta A$  changes are remarkably similar to those observed on the microsecond time scale concomitant with C—C bond fragmentation of the amino alcohol radical cation **12** (eq 3).<sup>14</sup> On the basis of this similarity, the 460 nm decay is assigned to disappearance of charge separated state **6** and the 370 nm rise is assigned to the appearance of  $\alpha$ -amino radical complex **7**. The rapid component ( $\leq 30 \text{ ps}$ ) of the  $\Delta A$  increase at observed at 360 nm is also consistent with Scheme 1, since initial MLCT photoexcitation of **1** produces **5** which has a characteristic absorption band at 370 nm (due to  $\text{bpy}^{*+}$ ) as shown in Figure 1a. The  $\text{bpy}^{*+}$  chromophore is then unaltered as **5** relaxes to **6** via forward electron transfer.

The kinetic model in Scheme 1 indicates that disappearance of **6** and appearance of **7** will occur with the same observed first-order rate,  $k_{\text{obs}} = k_{\text{BET}} + k_{\text{BF}}$ . Consistent with this expectation, both the 370 nm rise and the 460 nm decay fit well to a single exponential rise or decay function with  $k_{\text{obs}} = 4.0 \times 10^8 \text{ s}^{-1}$ . The rate of C—C bond fragmentation of the diamine radical cation in **6** can now be deduced by the expression,  $k_{\text{BF}} = k_{\text{obs}} - k_{\text{BET}}$ . Evaluation of this expression using  $k_{\text{BET}} = 1.0 \times 10^8 \text{ s}^{-1}$  (which is taken from the decay rate

of charge separated state **11**, eq 2)<sup>27</sup> and  $k_{\text{obs}} = 4.0 \times 10^8 \text{ s}^{-1}$  leads to  $k_{\text{BF}} = 3.0 \times 10^8 \text{ s}^{-1}$ .

The free energy change for C–C bond fragmentation of the diamine radical cation in **6** ( $\Delta G_{\text{CC}^{++}}$ ) can be estimated by the expression,  $\Delta G_{\text{CC}^{++}} \approx \Delta G_{\text{CC}} + F(\Delta E_{1/2})$ ,<sup>28,29</sup> where  $\Delta G_{\text{CC}}$  is the free energy change for C–C bond homolysis of the neutral diamine,  $F$  is Faraday's constant, and  $\Delta E_{1/2}$  is the half-wave potential for reduction of iminium ion **8** minus the half-wave potential for oxidation of the diamine ligand in complex **1**. Reasonable estimates for these terms are  $\Delta G_{\text{CC}} \approx +38 \text{ kcal/mol}$ <sup>30</sup> and  $\Delta E_{1/2} \approx -1.79 \text{ V}$ ,<sup>33</sup> and by using these values we estimate  $\Delta G_{\text{CC}^{++}} \approx -3 \text{ kcal/mol}$ , i.e., C–C bond fragmentation of the diamine radical cation is weakly exothermic. The free energy of activation for bond fragmentation of the diamine radical cation in **6** is  $\Delta G_{\text{CC}^{++}}^{\ddagger} \approx 6 \text{ kcal/mol}$ , which is substantial, given that the reaction is estimated to be weakly exothermic. This implies that there is a moderate "intrinsic barrier" (or reorganization free energy) associated with the C–C bond fragmentation reaction.<sup>29b</sup> This intrinsic barrier may be associated with the stereoelectronic demands of the transition state or with solvent repolarization that accompanies redistribution of positive charge concomitant with lengthening of the C–C bond.<sup>35,36</sup>

In conclusion, the nanosecond and picosecond transient absorption studies of aniline substituted Re(I) complexes **1** and **2** has allowed direct determination of the rate of C–C bond fragmentation of a diamine radical cation. This weakly exothermic fragmentation reaction is very rapid and competes favorably with back electron transfer in the intramolecular charge separated state. Now that the bond fragmentation reaction of the diamine radical cation "clock" has been calibrated, this system may be applied to probe the dynamics of back electron transfer in intramolecular charge separated states or geminate radical ion pairs formed by photoinduced electron transfer.

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- (22) The driving force for forward electron transfer ( $\Delta G_{\text{FET}}$ ) is approximately  $-0.40 \text{ eV}$  for **1** and **2** (see ref 13).
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- (24) The picosecond transient absorption decay was analyzed under the assumption that  $\Delta A_{\infty} = 0$  which is based on the nanosecond transient absorption kinetics.
- (25) A transient that could be assigned to the MLCT state was not observed in the picosecond transient absorption studies of **1** and **2**. We conclude that either (1) forward electron transfer (e.g., **5**  $\rightarrow$  **6**, Scheme 1) is exceedingly rapid ( $k \geq 2 \times 10^{10} \text{ s}^{-1}$ ), or (2) a clearly distinguishable change in the transient absorption spectrum does not accompany forward electron transfer. The former possibility is not unlikely given that  $\Delta G_{\text{FET}} \approx -0.4 \text{ eV}$  and the close proximity ( $\approx 5 \text{ \AA}$ ) of the aniline donor to the Re center.
- (26) The decision to carry out the picosecond studies at selected wavelengths was dictated by several factors. First, **1** undergoes irreversible photochemistry with a high quantum efficiency thereby limiting the amount of data that can be acquired with a finite supply of the material (0.4 g of **1** was used for the picosecond studies presented herein). Second, since extensive nanosecond transient absorption data was available on metal complexes **1–3** and reactive intermediates **12** and **13**, we felt that it was a good probability that collection of temporally resolved picosecond transient absorption data at selected near-UV and mid-visible wavelengths would allow us to elucidate the dynamics of C–C bond fragmentation in **1**, the primary objective of the present study.
- (27) Additional evidence supporting the premise that model complex **2** provides a good estimate for  $k_{\text{BET}}$  in **1** comes from a recently published study<sup>13</sup> of a substituted Re(I) complex that is identical in structure to **1** except that the piperidino ring is replaced by an OH group. Flash photolysis studies of this amino alcohol complex indicate that  $k_{\text{BET}} \approx 1 \times 10^8 \text{ s}^{-1}$  in this system as well.
- (28) The expression  $\Delta G_{\text{CC}^{++}} \approx \Delta G_{\text{CC}} + F(\Delta E_{1/2})$  is based on a thermodynamic cycle. See ref 29 for details.
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