

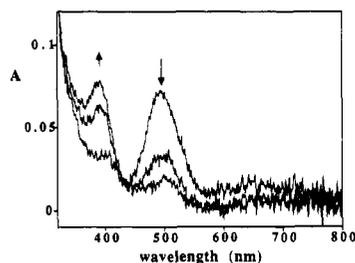
# First Direct Structural Information on a Reactive $\sigma\pi^*$ Excited State: Time-Resolved UV–Vis and IR Spectroscopic Study of $\text{Re}(\text{benzyl})(\text{CO})_3(\text{iPr-DAB})$

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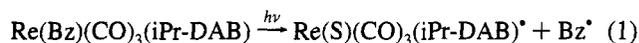
Covalent metal–alkyl or metal–metal bonds in organometallic compounds that contain an electron-accepting ligand in their coordination sphere are often prone to photochemical homolytic dissociation.<sup>1</sup> Metal–metal bonded complexes  $\text{L}_n\text{M}-\text{Re}(\text{CO})_3(\alpha\text{-diimine})^1$  ( $\text{L}_n\text{M} = (\text{CO})_5\text{Mn}, (\text{CO})_5\text{Re}, \text{Ph}_3\text{Sn}, (\text{CO})_4\text{Co}$ ) and  $(\text{OC})_5\text{MnRu}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})^2$  and metal–alkyl complexes  $\text{Ru}(\text{X})(\text{iPr})(\text{CO})_2(\alpha\text{-diimine})^3$  ( $\text{X} = \text{halide}$ ),  $\text{M}(\text{R})(\text{CO})_3(\alpha\text{-diimine})^{4-6}$  ( $\text{M} = \text{Mn}, \text{Re}$ ),  $\text{Ir}(\text{R})(\text{CO})(\text{PAR}_3)_2\text{-}(\text{mnt})$ ,<sup>7</sup>  $\text{Pt}(\text{Me})_4(\alpha\text{-diimine})$ ,<sup>8</sup> and  $\text{ZnR}_2(\alpha\text{-diimine})$ <sup>9</sup> are representative examples. Bond homolysis from a  $\sigma\pi^*$  excited state is usually assumed<sup>1,2,5-12</sup> to be the primary photochemical step involved. This excited state originates in excitation of an electron from the to-be-split  $\sigma$  bond to the  $\pi^*$  orbital of the acceptor ligand, usually  $\alpha$ -diimine. Except for  $\text{Pt}(\text{Me})_4(\alpha\text{-diimine})$  and  $\text{ZnR}_2(\alpha\text{-diimine})$  complexes,<sup>9,13</sup> the  $\sigma \rightarrow \pi^*$  transition was not observed spectroscopically and the  $\sigma\pi^*$  state may only be populated nonradiatively from optically excited MLCT states.<sup>1</sup> Unusually long-lived emission from  $(\text{OC})_5\text{-MnRu}(\text{R})(\text{CO})_2(\alpha\text{-diimine})$ <sup>14</sup> as well as from  $\text{Ph}_3\text{SnRe}(\text{CO})_3\text{-}(\text{phen})$ ,  $(\text{CO})_5\text{ReRe}(\text{CO})_3(\text{phen})$ <sup>10,12</sup> and  $\text{Ir}[(8\text{-quinolyl})\text{diorganosilyl}]_3$  complexes<sup>15-17</sup> is assumed to originate in the  $\sigma(\text{M}-\text{M})\pi^*$  excited state. Despite these encouraging results, direct detection of a  $\sigma\pi^*$  excited state as an intermediate in the photochemical homolysis of a metal–ligand bond and its



**Figure 1.** Time-resolved UV–vis spectra of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  in toluene measured at 30, 230, and 430 ns after the excitation. Spectra are corrected for the bleached ground state absorption.

spectroscopic characterization have, so far, been missing, leaving the nature and dynamics of the putative  $\sigma\pi^*$  excited state largely unknown.

Hence, we have undertaken a nanosecond to microsecond time-resolved UV–Vis and IR spectroscopic study of the  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  complex<sup>18</sup> ( $\text{Bz} = \text{benzyl}$ ;  $\text{iPr-DAB} = N,N'$ -diisopropyl-1,4-diazabutadiene,  $\text{iPrN}=\text{CHCH}=\text{NiPr}$ ), which undergoes an efficient homolysis of the  $\text{Re}-\text{Bz}$  bond<sup>5,6</sup> upon excitation into its MLCT visible absorption band;  $\text{S} = \text{solvent}$ :



Degassed toluene and *n*-heptane solutions were used to obtain the UV–vis and IR spectra, respectively, following laser pulse excitation at 532 nm, 7–10 ns (fwhm) directed to the MLCT absorption band ( $\lambda_{\text{max}} = 441 \text{ nm}$ ,  $\epsilon = 4900 \text{ M}^{-1} \text{ cm}^{-1}$ ; 485 nm (sh) in toluene) of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$ . Formation of a photogenerated intermediate was found to take place very rapidly, being complete within the excitation pulse. This intermediate exhibits an absorption band in the visible spectral region at 500 nm (Figure 1) and  $\nu(\text{CO})$  IR features at 2015  $\text{cm}^{-1}$  and approximately at 1910  $\text{cm}^{-1}$  (broad); because of overlap with the bands of the parent it is difficult to disentangle the low-frequency region (Figure 2b). This intermediate decays directly into a product characterized by absorption band at 390 nm in the UV region (Figure 1) and by IR features at about 2023, 1932, and 1898  $\text{cm}^{-1}$ . The latter two apparent maxima probably belong to a single broad band (Figure 2c). The UV–vis and IR experiments show that the intermediate decay and the product formation follow the same first-order kinetics. This is demonstrated in Figure 3 by the kinetic traces of the IR absorbance measured at IR frequencies corresponding to the maximum absorption of the transient, Figure 3a, and of the photoproduct, Figure 3b. The lifetime of 250 ns ( $\pm 10\%$ ) determined from the UV–vis spectra agrees well with that obtained from the IR experiment, 210–290 ns.<sup>19</sup> No evidence for a return to the ground state was found as shown by the constant intensity of the negative bands due to bleached ground state absorption over the time interval studied; compare Figure 2, parts b and c. In both types of experiments, transient formation was quenched by dioxygen, suggesting that the transient is an excited state.

The product absorption band at 390 nm is assigned to the  $\text{Re}(\text{S})(\text{CO})_3(\text{iPr-DAB})^*$  radical. It is diagnostic for the  $\text{Re}(\text{S})\text{-}(\text{CO})_3(\alpha\text{-diimine})$  radicals, as was shown by spectroelectrochemical studies<sup>20-22</sup> of  $\text{Re}(\text{X})(\text{CO})_3(\alpha\text{-diimine})$  and by flash

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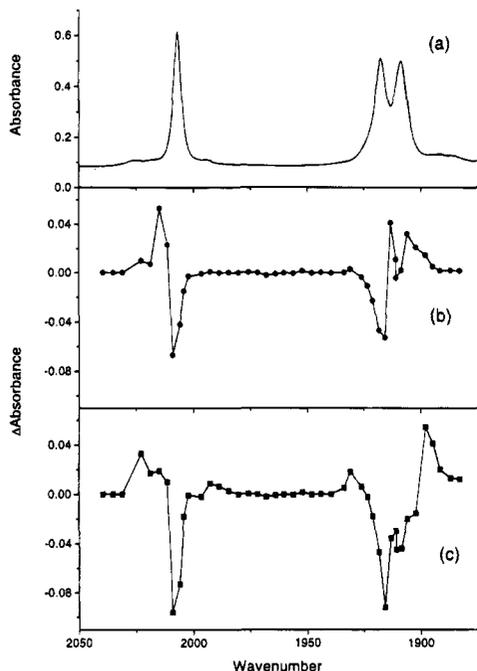
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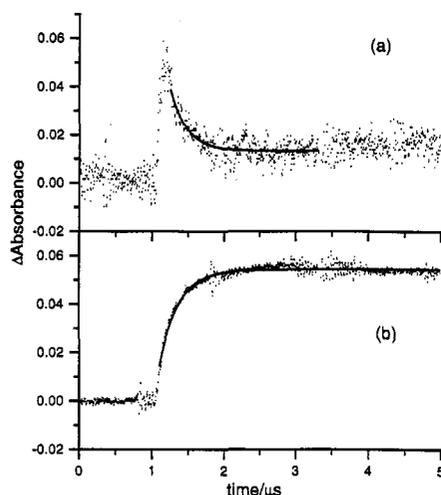
(19) Variation of the lifetime with the probe IR frequency is due to the presence of a small amount of an unidentified byproduct; note also the weak IR peak at about 1993  $\text{cm}^{-1}$  that has different kinetic behavior from the bands at 2023, 1932, and 1898  $\text{cm}^{-1}$ .

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**Figure 2.** (a) FTIR spectrum of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  in *n*-heptane. (b) Difference time-resolved IR spectrum measured 100 ns after excitation. (c) Difference time-resolved IR spectrum measured 3.5  $\mu\text{s}$  after excitation. Sample concentration  $5 \times 10^{-4}$  M, optical path length = 2 mm.



**Figure 3.** Kinetic traces of the IR absorbance of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  in *n*-heptane measured after 532 nm, 10 ns excitation: (a) immediate formation and subsequent decay of the primary intermediate monitored at  $2014.9 \text{ cm}^{-1}$ ,  $\tau = 210 \text{ ns}$ ; (b) photoproduct formation ( $\tau = 260 \text{ ns}$ ) monitored at  $1898 \text{ cm}^{-1}$ .

photolysis of  $\text{L}_n\text{MRe}(\text{CO})_3(\text{iPr-DAB})$  complexes<sup>23</sup> which are known to produce  $\text{Re}(\text{S})(\text{CO})_3(\alpha\text{-diimine})^*$  radicals upon reduction and irradiation, respectively. This is further supported by comparison of the product IR spectrum (Figure 2c) with IR spectra of electrochemically produced  $\text{Re}(\text{S})(\text{CO})_3(\text{iPr-DAB})^*$  radicals<sup>6,20</sup> which show IR bands at 2007 and 1891/1875 (double band)  $\text{cm}^{-1}$  ( $\text{S} = \text{nPrCN}$ ) and at 2005 and 1894 (broad)  $\text{cm}^{-1}$ ,  $\text{S} = \text{THF}$ . The low-frequency shift from the frequencies measured by TRIR is caused both by coordination of the donor solvent molecule in the electrochemically produced radicals and by a general solvent effect found even for  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  itself ( $-9 \text{ cm}^{-1}$  going from *n*-heptane to  $\text{THF}^{18}$ ).

The primarily formed intermediate corresponds to the excited state from which the  $\text{Bz-Re}$  bond homolysis occurs, *i.e.*, to the  $\sigma\pi^*$  excited state. The position and lifetime of its transient absorption at 500 nm, tentatively assigned to the  $d_\pi \rightarrow \pi^*$  (*i.e.*,  $\sigma\pi^* \rightarrow \text{MLCT}$ ) transition, distinguishes the  $\sigma\pi^*$  state both from the  $\text{Re}(\text{S})(\text{CO})_3(\text{iPr-DAB})^*$  radical, which does not absorb significantly in the visible spectral region,<sup>6,21,23</sup> and from the  $\text{Re} \rightarrow \text{DAB}$  MLCT state, which, in complexes where it is the lowest excited state, is very short-lived ( $< 10 \text{ ns}$ ), exhibiting just a broad and very weak absorption in the visible. This was demonstrated, *e.g.*, for  $\text{Re}(\text{Me})(\text{CO})_3(\text{R-DAB})^{5,6}$  and  $\text{Re}(\text{X})(\text{CO})_3(\text{aryl-DAB})^{22}$ . The pattern of the  $\nu(\text{CO})$  spectral bands indicates that the *fac*-tricarbonyl geometry of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  is retained in its  $\sigma\pi^*$  excited state, since the stretching frequencies show only a very small shift from the ground state values, 2007, 1918, 1909  $\text{cm}^{-1}$  (Figure 2a). This observation indicates that excitation of an electron from the  $\sigma(\text{Re-Bz})$  to the  $\pi^*(\text{DAB})$  orbital does not affect significantly the total electron density on the Re atom, the diminished electron donation from Bz being compensated by decreased  $\pi$ -backbonding to the iPr-DAB ligand and increased  $\text{N} \rightarrow \text{Re}$   $\sigma$ -donation. Obviously, the  $\sigma\pi^*$  excited state of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  is rather different from the  $d_\pi\pi^*$  MLCT excited states of analogous  $\text{Re}(\text{L})(\text{CO})_3(\alpha\text{-diimine})$  species where depopulation of the  $d(\pi)$  orbitals is known to cause positive shifts of the  $\nu(\text{CO})$  frequencies as large as  $66 \text{ cm}^{-1}$ , as was found for  $\text{Re}(\text{Cl})(\text{CO})_3(4,4'\text{-bipyridyl})_2^{24}$  and  $\text{Re}(\text{Cl})(\text{CO})_3(2,2'\text{-bipyridyl})^{25}$ .

It is noteworthy that neither IR nor visible transient absorption assignable to the  $\sigma\pi^*$  excited state has been observed after the 532 nm laser pulse excitation of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  in the nucleophilic solvents  $\text{CH}_3\text{CN}$  and  $\text{THF}$ . In these solvents, the formation of the  $\text{Re}(\text{S})(\text{CO})_3(\text{iPr-DAB})^*$  radical is complete already within the 7 ns excitation pulse, indicating a dramatic drop in the  $\sigma\pi^*$  lifetime. A similar, although less dramatic, effect was found for  $\text{Ir}[(8\text{-quinolyl})\text{diorganosilyl}]_3$  complexes.<sup>15-17</sup>

In conclusion, the  $\sigma\pi^*$  excited state of  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  has been found to be populated efficiently and rapidly from the optically excited MLCT state. The  $\sigma\pi^*$  state is the immediate precursor to the photochemically formed radicals. Its long lifetime and well-defined vibrational and electronic absorption bands show that it is, at least in non-nucleophilic solvents, a bound state with a well-defined energetic minimum on its potential energy surface. The  $\sigma\pi^*$  excited state may be approximately viewed as a weakly bound biradical  $\text{Bz}^+\text{Re}^-(\text{CO})_3(\text{iPr-DAB}^{\bullet-})$ , the  $\text{Bz}^+$  radical ligand being coordinated by a one-electron bond. The  $\text{Re-Bz}$  bond homolysis<sup>6</sup> occurs on a time scale of hundreds of nanoseconds only after the thermal equilibration of the  $\sigma\pi^*$  state. The surprising stability of the  $\sigma\pi^*$  state with respect to the return to the ground state may be explained by its presumed spin-triplet character and by small excited state distortion.<sup>14</sup> The electron-deficient  $\text{Bz-Re}^1$  bond may easily be attacked by nucleophiles.

Finally, it should be noted that the photochemical  $\text{Re-Bz}$  bond homolysis in  $\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})$  exhibits<sup>6</sup> all the features (high, temperature- and excitation-wavelength-independent, quantum yield) characteristic of the whole family of photoreactive metal-alkyl and metal-metal diimine complexes. Hence, the conclusions on the  $\sigma\pi^*$  excited state may be easily generalized. The differences in the photoreactivity of individual complexes of this class then appear to be caused by different relative energies<sup>5,6</sup> of the MLCT and  $\sigma\pi^*$  states, by the extent of the bond labilization in the  $\sigma\pi^*$  state, and by possible involvement of additional LLCT or LF excited states.

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