First Direct Structural Information on a Reactive sigma-\pi^* Excited State: Time-Resolved UV-VIS and IR Spectroscopic Study of Re(Benzyl) (CO)C3(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.\(^1\) Metal–metal bonded complexes \(\text{LM} = \{\text{CO}\}^n\text{Re}-\text{Re}\{\text{CO}\}^n\text{L}\) \(^5\) (\(\text{L} = \{\text{CO}\}^n\text{Re} \cdots \text{Re}\{\text{CO}\}^n\text{L}\) and \(\text{OC}_2\text{MnRu}(\text{CO})\_2(\text{a}-\text{diimine})^2\) and metal–alkyl complexes \(\text{Ru}(\text{X})\{\text{IPr}\}(\text{CO})_2(\text{a}-\text{diimine})^3\) are representative examples. Bond homolysis from a \(\sigma^*\) excited state is usually assumed\(^1\),\(^2\),\(^5\),\(^6\) to be the primary photochemical step involved. This excited state originates in excitation of an electron from the to-be-split bond to the \(\pi^*\) orbital of the acceptor ligand, usually \(\alpha\)-diimine. Except for \(\text{Pt}(\text{Me})_4(\text{a}-\text{diimine})^5\), \(\text{Re}(\text{CO})_3(\text{a}-\text{diimine})^5\), \(\text{Ru}(\text{X})\{\text{IPr}\}(\text{CO})_2(\text{a}-\text{diimine})^3\) and \(\text{MnRu}(\text{CO})_2(\text{a}-\text{diimine})^2\), 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 \(\tau(\text{CO})\) IR features at 2015 cm\(^{-1}\) and approximately at 1910 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 1910 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 1910 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 1910 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 1910 cm\(^{-1}\) (broad); because of overlap with the bands of the parent it is difficult to disentangle the low-frequency region (Figure 2b).
The primarily formed intermediate corresponds to the excited state from which the Bz-Re bond homolysis occurs, i.e., to the \( \sigma^* \) excited state. The position and lifetime of its transient absorption at 500 nm, tentatively assigned to the \( d_\alpha \rightarrow \pi^* \) (i.e., \( \sigma^* \rightarrow \text{MLCT} \)) transition, distinguishes the \( \sigma^* \) state both from the Re(S)(CO)\(_3\)(iPr-DAB)\(^{+}\) radical, which does not absorb significantly in the visible spectral region,\(^{6,22,23}\) and from the Re \( \rightarrow \) DAB MLCT state, which, in complexes where it is the lowest excited state, is very short-lived (<10 ns), exhibiting just a broad and very weak absorption in the visible. This was demonstrated, e.g., for Re(Me)(CO)\(_3\)(R-DAB)\(^{5,6}\) and Re(X)(CO)\(_3\)(aryl-DAB).\(^{22}\) The pattern of the \( \nu(CO) \) spectral bands indicates that the fac-tricarbonyl geometry of Re(Bz)(CO)\(_3\)(iPr-DAB) is retained in its \( \sigma^* \) excited state, since the stretching frequencies show only a very small shift from the ground state values, 2007, 1918, 1909 cm\(^{-1}\) (Figure 2a). This observation indicates that excitation of an electron from the \( \sigma \) (Re=Bz) to the \( \pi^* \)(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 \( \pi \) \( \rightarrow \) Re \( \sigma \)-donation. Obviously, the \( \sigma^* \) excited state of Re(Bz)(CO)\(_3\)(iPr-DAB) is rather different from the \( d_\alpha, \pi^* \) MLCT excited states of analogous Re(L)(CO)\(_3\)(a-diimine) species where depopulation of the \( d(\pi) \) orbitals is known to cause positive shifts of the \( \nu(CO) \) frequencies as large as 66 cm\(^{-1}\), as was found for Re(Cl)(CO)\(_3\)(4,4'-bipyridy1)\(^{24}\) and Re(Cl)(CO)\(_3\)(2,2'-bipyridy1).\(^{25}\)

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

In conclusion, the \( \sigma^* \) excited state of Re(Bz)(CO)\(_3\)(iPr-DAB) has been found to be populated efficiently and rapidly from the optically excited MLCT state. The \( \sigma^* \) 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 \( \sigma^* \) excited state may be approximately viewed as a weakly bound biradical Bz\(^{+}\)Re\(^{1}\)(CO)\(_3\)(iPr-DAB\(^{+}\)), the Bz\(^{+}\) radical ligand being coordinated by a one-electron bond. The Re-Bz bond homolysis occurs on a time scale of hundreds of nanoseconds only after the thermal equilibration of the \( \sigma^* \) state. The surprising stability of the \( \sigma^* \) 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.\(^{14}\) The electron-deficient Bz-Re\(^{1}\) bond may easily be attacked by nucleophiles.

Finally, it should be noted that the photochemical Re-Bz bond homolysis in Re(Bz)(CO)\(_3\)(iPr-DAB) exhibits all the features (high, temperature- and excitation-wavelength-independent, quantum yield) characteristic of the whole family of photoactive metal-alkyl and metal-metal diimine complexes. Hence, the conclusions on the \( \sigma^* \) excited state may be easily generalized. The differences in the photoactivity of individual complexes of this class then appear to be caused by different relative energies\(^{6,8}\) of the MLCT and \( \sigma^* \) states, by the extent of the bond labilization in the \( \sigma^* \) state, and by possible involvement of additional LLCT or LF excited states.

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Figure 2. (a) FTIR spectrum of Re(Bz)(CO)\(_3\)(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 \( \mu \)s after excitation. Sample concentration \( 5 \times 10^{-4} \) M, optical path length = 2 mm.

Figure 3. Kinetic traces of the IR absorbance of Re(Bz)(CO)\(_3\)(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 cm\(^{-1}\), \( \tau = 210 \) ns; (b) photoproduct formation (\( \tau = 260 \) ns) monitored at 1898 cm\(^{-1}\).