Photochemistry of ReR(CO)$_3$(Pr^i-dab) (R = Me, Et, Bn; dab = 1,4-diazabuta-1,3-diene): Homolysis of the Re–R Bond, its Dependence on R and Evidence for the Reactive σ$_b$π* State from Transient Absorption Spectra

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From quantum yield and nanosecond flash photolysis data and UV–PE spectra it is concluded that metal-to-ligand charge transfer (MLCT) excitation of the complexes ReR(CO)$_3$(Pr^i-dab) (R = Me, Et, Bn) only leads to efficient homolysis of the metal–alkyl bond if R = Et or Bn, when the reactive σ$_b$π* state is close in energy to the MLCT states.

Homolytic splitting of the metal–metal bond of the complexes L$_n$MM^i(CO)$_3$(α-diimine) [L$_n$M = (CO)$_5$Mn, (CO)$_4$Co; M^i = Mn, Re][1–3] by excitation with visible light has been explained by surface crossing from the MLCT states to either ^{3}σ$_b$π* or ^{3}σ$_b$σ* states.[4,5] A reaction from the ^{3}σ$_b$π* state, as for R$_2$Zn(α-diimine),[6] is most likely since the high quantum yields (> 0.2) indicate a strong coupling between the MLCT and reactive states.[5] The UV–PE spectra of these metal–metal bonded complexes show that the σ$_b$(M–M^i) orbital has a lower ionisation energy than the d$_π$(M^i) orbitals,[7] which places the reactive σ$_b$π* state at a lower energy than the non-reactive d$_π$π* (MLCT) states. In order to influence the photoreactivity by varying the relative energies of these reactive and non-reactive states, we have studied the photochemistry of the complexes ReR(CO)$_3$(α-diimine) (R = Me, Et, Bn).[8]

Quite recently, Schanze and coworkers have shown that the complexes ReR(CO)$_3$(bpy) (R = Me, Bn; bpy = 2,2′-bipyridine) behave similarly to metal–metal bonded compounds and photodecompose with quantum yields close to unity.[9] However, a different behaviour has been observed by us for the complexes ReR(CO)$_3$(R^1-dab) (R, R^1 = alkyl; dab = 1,4-diazabuta-1,3-diene), their photoreactivity showing a strong dependence on R. This is demonstrated for the two representative complexes ReR(CO)$_3$(Pr^i-dab) (R = Me, Et).

The complexes, which were prepared by published methods,[10] were irradiated into their visible absorption band (Fig. 1).† The MLCT character of this band was evident from the resonance enhancement of the Raman bands belonging to v$_s$(CO) and v$_s$(CN) of the Pr^i-dab ligand. Irradiation gave rise to the formation of radicals R· and Re$^+$(CO)$_3$(Pr^i-dab·$^-$), which were trapped by Bu^{t}NO and identified as adducts by EPR spectroscopy.[11] The Re$^+$(CO)$_3$(Pr^i-dab·$^-$) radicals could not be detected as persistent radicals since they underwent similar coupling reactions to the corresponding ZnR(Bu^t-dab·$^-$) radicals.‡[6]

The quantum yield of the photodecomposition reaction‡ showed a remarkable dependence on the alkyl group. For R = Et it was close to unity and was temperature and wavelength independent (Table 1), like the metal–metal bonded complexes and the bpy-compounds ReR(CO)$_3$(bpy).[9] The complex Re(Me)(CO)$_3$(Pr^i-dab) showed a completely different behaviour. Its photodecomposition quantum yield was low and temperature dependent (Table 1, Fig. 1), pointing to a situation in which the reactive σ$_b$π* state is at a higher energy than the relaxed MLCT state. The wavelength dependence (Table 1, Fig. 1) showed that there was also a direct crossing from higher excited states to the reactive σ$_b$π* state.

From the temperature dependence (T = 253–283 K) of the quantum yield, the following activation energies were derived: E_a(457.9 nm) = 7.5 ± 0.8 kJ mol^{-1}, E_a (488.0 nm) = 8.8 ± 0.4 kJ mol^{-1} and E_a (501.7 nm) = 10.3 ± 0.4 kJ mol^{-1}. The increase in activation energy with decreasing excitation energy is in agreement with the reactive σ$_b$π* state being at a higher energy than the MLCT state.

The different behaviour of the Et and metal–metal bonded complexes on one side and the Me-complex on the other, is clearly connected with the energy difference between the MLCT and σ$_b$π* states. Contrary to the metal–metal bonded complexes, the UV–PE spectrum of Re(Me)(CO)$_3$(Pr^i-dab) shows the σ$_b$(Re–Me) orbital at a higher ionisation energy (8.50 eV) than the d$_π$(Re) orbitals (7.25, 7.80 eV). The σ$_b$π* states of this complex will therefore be at higher energy than the MLCT states. This explains the low, temperature dependent quantum yield of the homolysis reaction for this complex. Going from R = Me to Et the ionisation energy of the σ$_b$(Re–R) orbital will decrease and the σ$_b$π* and d$_π$π* states will become closer in energy.[12] Unfortunately, the Et-complex was thermally too unstable to provide reliable UV–PE spectra.

Further evidence for the involvement of a reactive σ$_b$π* state was presented by the transient absorption spectra.§ For the non-reactive complex Re(Me)(CO)$_3$(Pr^i-dab) a similarly short-lived (τ < 20 ns) transient absorption of the MLCT state was observed as for the corresponding halide (X) complexes ReX(CO)$_3$(Pr^i-dab). However, the complex Re(Bn)-(CO)$_3$(Pr^i-dab), which reacts with a quantum yield close to unity just as the Et-analogue, produced a rather long-lived transient in cyclohexane and toluene (λ$_{max}$ ≈ 500 nm, τ = 282 ± 14 ns in toluene) which photodecomposed into radicals.
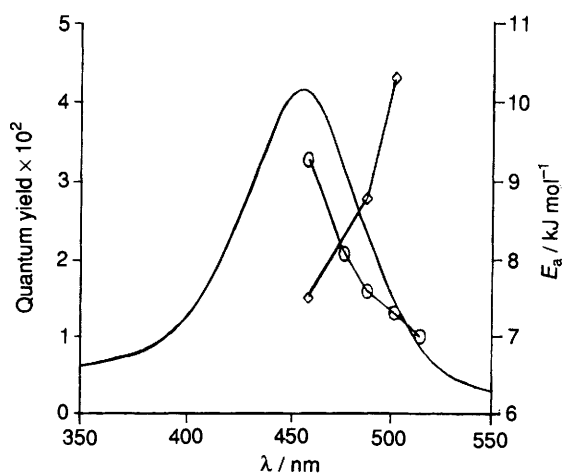

Fig. 1 Dependence of quantum yield Φ (○) (273 K) and activation energy E_a (◇) on the excitation wavelength for the homolysis reaction of Re(Me)(CO)$_3$(Pr^i-dab) in THF

Table 1 Quantum yields^a for the homolysis reaction of ReR(CO)$_3$(Pr^i-dab) in THF as a function of excitation wavelength

	R	
λ/nm	Me (× 10^2)	Et
457.9	3.28 (± 0.12)	0.97 (± 0.02)
476.5	2.09 (± 0.12)	—
488.0	1.60 (± 0.03)	0.98 (± 0.01)
501.7	1.31 (± 0.01)	1.06 (± 0.01)
514.5	1.00 (± 0.01)	0.99 (± 0.04)

^{a} Average values of three measurements; T = 273.0 K.

This transient was not emissive. In THF the complex photodecomposed into radicals much more rapidly and the transient could not even be observed in the picosecond transient absorption spectra ($\tau < 30$ ps).§ Solvent coordination probably accelerates the homolysis of the weak Re–Bn bond of the complex in its $\sigma_b\pi^*$ state. A similar solvent dependency of the lifetime of a proposed $\sigma_b\pi^*$ state has recently been observed by Djurovich and Watts for *N,Si*-chelated Ir^{III} complexes.[13]

The Netherlands Foundation for Chemical Research (SON) and the Netherlands Organisation for the Advancement of Pure Research (NWO) are thanked for their financial support.

Received, 23rd July 1993; Com. 3/04383E

Footnotes

† UV–VIS data for the complexes ReR(CO)$_3$(Pr^i-dab) in THF (λ_{max} in nm; ε in mol^{-1} dm^3 cm^{-1} in parentheses): R = Me, 455 (7150); R = Et, 460 (7400); R = Bn, 432 (4950).

‡ This is the quantum yield for the disappearance of the Re–R complex. The products are a C–C coupled Re-dimer (X-ray structure to be published) and a coupling product of the R· and Re$^+$(CO)$_3$(Pr^i-dab·$^-$) radicals, which has not yet been structurally characterized.

§ In the nanosecond flash photolysis experiments, a sample with a maximum optical density (o.d.) of 0.6 at the excitation wavelength was excited with 532 nm, 5 ns pulses (20 mJ per pulse). The solution was flowed through the spectral cell after each pulse. Picosecond flash photolysis experiments were carried out at the Canadian Centre for Picosecond Laser Spectroscopy (Montreal) with 532 nm, 30 ps pulses (2.5 mJ per pulse) on samples with a maximum o.d. of 0.5 at the excitation wavelength.

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