A new series of Re- and Ru-complexes having a lowest σπ* excited state that varies from reactive to stable and long lived

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Abstract:: The complexes Re(L)(CO)$_3$(α-diimine) and Ru(E)(E')(CO)$_2$(α-diimine), in which L and E/E' represent an alkyl group or metal fragment bound to the metal by a high-lying σ orbital, have a lowest ^{3}σπ* state from which they normally decompose into radicals. In the case of Re(benzyl)(CO)$_3$(iPr-DAB) the rate of the radical formation was found to be strongly dependent on the coordinating ability of the solvent. Decay to the ground state is slow due to a weak distortion of the complex in its ^{3}σπ* state. This weak distortion is evident from the time-resolved IR spectra, which show that the v(CO) vibrations hardly shift upon σ--->π* excitation. By the introduction of two σ-bonded groups (E and E') in Ru(E)(E')(CO)$_2$(α-diimine) the σ-bonding orbital becomes delocalised over Ru, E, E' and the α-diimine ligand and distortion in the ^{3}σπ* state is further decreased. As a result, the complex Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB) has, in a glass at 77 K, an emission lifetime of 264 μs, which is very long compared to those of related complexes having a lowest ^{3}MLCT state (e.g. τ= 300 ns for Ru(Cl)(Me)(CO)$_2$(iPr-DAB)). Contrary to these ^{3}MLCT states, the ^{3}σπ* state may thus vary from very labile and short lived to stable and very long lived depending on the strength and delocalisation of the σ bond.

INTRODUCTION

There has been considerable interest in the photophysics and photochemistry of complexes of the type Ru(α-diimine)$_3$$^{2+}$ and Re(L)(CO)$_3$(α-diimine)$^{n+}$ (n= 0,1; α-diimine= bpy, etc.), which are good photosensitizers for energy and electron transfer processes (ref.1-5). Most Re(L)(CO)$_3$(α-diimine)$^{n+}$ complexes have a lowest metal-to-ligand charge transfer (MLCT) excited state, but this character can easily be influenced by variation of L. Thus, the excited state changes to ligand-to-ligand charge transfer (LLCT) when L becomes e.g. an iodide (ref.6) or organic donor molecule (ref.3). In the case that L represents a metal fragment or alkyl group, that is to the metal by a relatively high-lying σ orbital, an electron may be excited from that σ orbital to a π* orbital of the diimine ligand. The lowest excited state then obtains ^{3}σπ* character (ref. 4,7). Although the corresponding σ-->π*(α-diimine) transitions are rather intense in the case of the alkyl complexes Zn(R)$_2$(α-diimine) (ref.8) and Pt(Me)$_4$(α-diimine) (ref.9), they may be only a weak contributor to the MLCT band of complexes such as Re(R)(CO)$_3$(α-diimine) (ref.7,10). In the latter case, the ^{3}σπ* state may then be populated by a surface crossing from an optically accessible MLCT state. In recent years we have studied in detail the photochemistry and photophysics of a series of metal-metal and metal-alkyl bonded complexes having such a ^{3}σπ* state in order to establish its bonding properties and dynamics. Normally, occupation of a ^{3}σπ* state leads to a homolytic splitting of the σ bond with the formation of radicals. In the case of the above mentioned Re(R)(CO)$_3$(α-diimine) complexes these are the radicals R· and the radical complexes Re(CO)$_3$(α-diimine)· (ref.7, 10). In the following sections we shall discuss the behaviour of the complexes Re(L)(CO)$_3$(α-diimine) (L= alkyl, metal fragment) and Ru(E)(E')(CO)$_2$(α-diimine) (E,E'= halide, alkyl, metal fragment), which have the general structures depicted in Fig.1.

Re-COMPLEXES: REACTIVE AND STABLE ^{3}σπ* STATES

Contrary to their Mn-analogues (ref.11) the complexes Re(L)(CO)$_3$(α-diimine)$^{n+}$ do not decompose from their lowest MLCT states. The Re complexes with a σ-bonded ligand L:are therefore only photoreactive
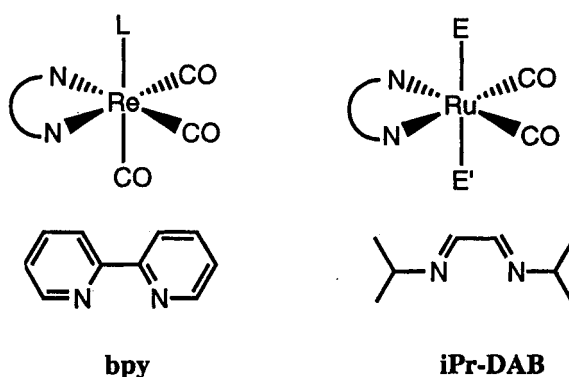
bpy   iPr-DAB

Fig.1 Structures of the complexes Re(L)(CO)₃(α-diimine)
and Ru(E)(E')(CO)₂(α-diimine) and of the α-diimine ligands.

when the $^3\sigma\pi^*$ state is lowest in energy or close in energy to the unreactive MLCT states. For the methyl complexes Re(Me)(CO)₃(α-diimine) the $^3\sigma\pi^*$ state is still at higher energy than the MLCT states and can only be reached by thermal activation after MLCT excitation (ref.7). As a result the quantum yield for the light-induced homolytic splitting of the Re-Me bond is only ca. 10^{-2} and this value increases with temperature. It is noteworthy that the activation energy, derived from this temperature dependence, decreases for Re(Me)(CO)₃(iPr-DAB) with the energy of excitation (ref.7). This implies that the activation energy does not originate in an energy barrier for cleavage of the Re-Me bond, but most likely in an avoided crossing between the vibronically coupled MLCT and $\sigma\pi^*$ states (ref.12). The reactive $^3\sigma\pi^*$ state shifts below the MLCT states when the methyl group is replaced by an ethyl or benzyl ligand as shown schematically in Fig.2. As a result, the quantum yield for the homolysis reaction of the complexes Re(R)(CO)₃(α-diimine) (R=Ethyl, Benzyl (Bz)) is near unity and wavelength and temperature independent (ref.7). For one of these complexes, viz. Re(Bz)(CO)₃(iPr-DAB), a combined time-resolved UV-Vis and IR spectroscopic study has been performed in different solvents (ref.7, 13). The picosecond absorption spectra in toluene showed a transient absorption at 500 nm formed already within the 30 ps excitation pulse. In the nanosecond spectra the same transient species was observed which transformed completely with a lifetime of 250 ns into a radical product absorbing at 390 nm (Fig.3). The solvent had a dramatic influence on the time-resolved spectra since the transient species was not observed upon irradiation of Re(Bz)(CO)₃(iPr-DAB) in THF or another coordinating solvent. Instead, the solvated radical Re(S)(CO)₃(iPr-DAB)· was already formed within 30 ps (ref.7). Transient formation was quenched by dioxygen, suggesting that the 500 nm band belongs to an excited state, in this case the $^3\sigma\pi^*$ state. In apolar solvents its lifetime is very long compared with that of the lowest ^{3}MLCT state of the Me-analogue Re(Me)(CO)₃(iPr-DAB) ($\tau < 10$ ns). Remarkably, this lifetime is completely determined by homolysis of the Re-benzyl bond since regeneration of the ground state molecule was not observed. This implies that the nonradiative decay to the ground state is very slow presumably because the $^3\sigma\pi^*$ state is only weakly distorted with respect to the ground state. Evidence for such a weak distortion was provided by the nanosecond time-resolved IR (TRIR) spectra, which showed that the ν(CO) bands of Re(Bz)(CO)₃(iPr-DAB) in its excited state nearly coincide with those of the complex in the ground state. The CO-vibrations merely shifted from 2009, 1916 and 1909 cm⁻¹ to 2015 and ca. 1909 cm⁻¹ upon $\sigma \text{---}> \pi^*$ excitation in n-heptane. Similar small shifts of the ν(CO) bands have recently been observed for the complex Ru(SnPh₃)₂(CO)₂(iPr-DAB) (ref.14) (*vide infra*).

The related metal-metal bonded complex Re(Mn(CO)₅)(CO)₃(iPr-DAB) (ref.15) showed very similar transient absorption spectra as Re(Bz)(CO)₃(iPr-DAB). Again, a transient peak showed up at ca. 500 nm, which transformed completely into the 390 nm band of the Re(S)(CO)₃(iPr-DAB)· radical. There was again no reformation of the ground state and the 500 nm band was also not observed in the weakly coordinating solvent 2-MeTHF.

From all Re complexes studied Re(SnPh₃)(CO)₃(4,4'-Me₂-bpy) was exceptional in being the only compound with a stable lowest $^3\sigma\pi^*$ state (ref.15). This enabled us to study its slow decay to the ground state under various conditions. The transient absorption band at 535 nm decayed at room temperature with a lifetime of 1100 ns in toluene and 500 ns in THF. Thus, the solvent also influences the lifetime of this stable $^3\sigma\pi^*$ state albeit to a much lesser extent than for the labile $^3\sigma\pi^*$ state of Re(Bz)(CO)₃(iPr-DAB). A similar solvent effect has been observed for Ir[(6-isopropyl-8-quinolyl)diorganosilyl]₃ (ref.16).
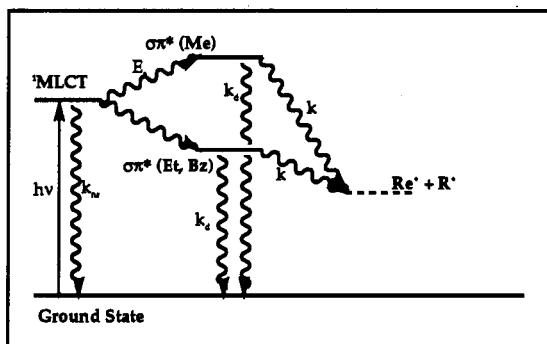
Fig. 2 Excited-state dynamics of the Re(R)(CO)$_3$(α-diimine) complexes.

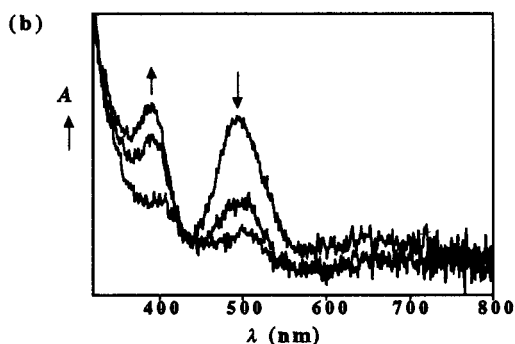Fig. 3 Nanosecond transient absorption spectra of Re(Bz)(CO)$_3$(iPr-DAB) in toluene at 30 ns, 230 ns and 430 ns after the 532 nm excitation pulse (corrected for the bleaching of the ground state absorption).

In a glass at 80K, the metal-metal bonded complexes Re(M'L$_n$)(CO)$_3$(α-diimine) (M'L$_n$= Mn(CO)$_5$, Re(CO)$_5$, SnPh$_3$) showed emission lifetimes of 1-100 µs (ref.15), which are much longer than those observed for the related halide (=X) complexes Re(X)(CO)$_3$(α-diimine) (τ< 4 µs) having a lowest ^{3}MLCT/XLCT excited state (ref.16). This difference is again mainly due to the much weaker distortion of these complexes in their $^3\sigma\pi^*$ state (*vide supra*) as reflected in a smaller Stokes shift and, hence, a lower value of k$_{nr}$ (ref.15). The above results clearly show that the properties of the $^3\sigma\pi^*$ state strongly depend on the metal fragment / alkyl group bonded to Re and on the solvent. Thus, the $^3\sigma\pi^*$ state has a lifetime of less than 30 ps for Re(Bz)(CO)$_3$(iPr-DAB) in THF at room temperature but lives longer than 1 µs in the case of Re(SnPh$_3$)(CO)$_3$(4,4'-Me$_2$-bpy) in toluene.

Ru-COMPLEXES: FIRST EVIDENCE OF A DELOCALISED $^3\sigma\pi^*$ STATE

In order to obtain a much greater variation in excited state character, we have extended our investigations to complexes of the type Ru(E)(E')(CO)$_2$(α-diimine) in which E and E' can be varied independently. Just as Re(Me)(CO)$_3$(iPr-DAB) (*vide supra*), the complex Ru(Cl)(Me)(CO)$_2$(iPr-DAB) has a lowest ^{3}MLCT state (ref.17). However, contrary to the Re-complex, the $^3\sigma\pi^*$ state is now too high in energy and, as a result, the Ru complex is photostable. Photoreactive complexes were obtained by replacing the methyl ligand by an isopropyl or benzyl group. The complexes Ru(I)(R)(CO)$_2$(iPr-DAB) (R= iPr, Bz) even decomposed photocatalytically since homolysis of the Ru-R bond was followed by an electron transfer chain reaction initiated by the Ru(I)(S)(CO)$_2$(iPr-DAB)· radicals (ref.18).

Recent time-resolved FT EPR measurements on some of these Ru(I)(R)(CO)$_2$(α-diimine) (R=iPr, Bz) complexes have shown that the radicals R· are formed from an excited state having triplet character (ref.19). Unfortunately, these ($^3\sigma\pi^*$) excited states were too short-lived to be detected with nanosecond time-resolved absorption spectroscopy.

The situation changes completely when both E and E' represent a σ-bonded ligand such as a methyl ligand or SnR$_3$ group. Recent DFT MO calculations on the model compounds Ru(Me)(SnH$_3$)(CO)$_2$(H-DAB) (ref.14) and Ru(SnH$_3$)$_2$(CO)$_2$(H-DAB) (ref.20) have shown that their HOMO's are delocalised σ orbitals, which consist of Ru(p$_z$), the antisymmetric sp^3(Sn)-sp^3(Me/Sn) combination, and the lowest π^* orbital of H-DAB. A similar strong mixing between H-DAB and Sn-Ru-Me/Sn orbitals was calculated for the LUMO. Because of this delocalised character, the σ--->π^* (HOMO--->LUMO) transitions of the model compounds were calculated to have high oscillator strengths. Accordingly, the intense lowest absorption bands of Ru(Me)(SnPh$_3$)(CO)$_2$(iPr-DAB) and Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB) were assigned to these σ(Sn-Ru-Me/Sn)--->π^*(iPr-DAB) transitions and the lowest excited state to $^3\sigma\pi^*$ (ref.14).

A detailed study of the photochemistry of a series of Ru(E)(E')(CO)$_2$(iPr-DAB) (E,E'= Me, SnPh$_3$, PbPh$_3$, GePh$_3$, Mn(CO)$_5$, Re(CO)$_5$) complexes showed that one of the Ru-E/E' bonds is broken homolytically and that this bond breaking is highly selective (ref.21). Thus, irradiation of Ru(Me)(Mn(CO)$_5$)(CO)$_2$(iPr-DAB)
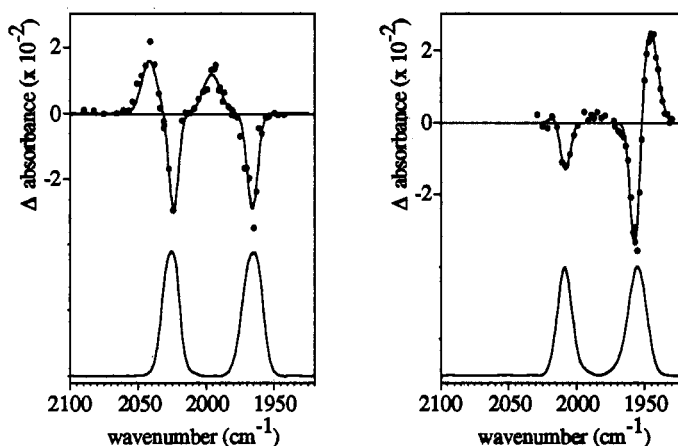
Fig. 4 TRIR and FTIR spectra of Ru(Cl)(SnPh₃)(CO)₂(iPr-DAB)
(left) and Ru(SnPh₃)₂(CO)₂(iPr-DAB) (right) at 77 K in nPrCN.
The lower spectra are FTIR ground state spectra, the upper spectra
are difference TRIR spectra obtained immediately after the 355 nm excitation.

caused the cleavage of the Ru-Mn bond, whereas the Ru-Me bond was broken in the case of Ru(Me)(SnPh₃)(CO)₂(iPr-DAB). With the exception of Ru(SnPh₃)₂(CO)₂(iPr-DAB) and Ru(SnPh₃)-(GePh₃)(CO)₂(iPr-DAB) the homolysis reactions proceeded so rapidly that the reactive $^3\sigma\pi^*$ state could not be observed with nanosecond transient absorption spectroscopy at room temperature.The complex Ru(SnPh₃)₂(CO)₂(iPr-DAB) decomposed rather slowly (τ= 1 μs at room temperature) from its $^3\sigma\pi^*$ state with a quantum yield of 0.23 at 290 K and an activation energy of 1450 cm⁻¹. The same activation energy was derived from the temperature-dependent emission lifetime (ref.14), which indicates that the Ru-Sn bond homolysis accounts fully for the thermally activated component of the nonradiative decay from the $^3\sigma\pi^*$ state. Apparently, the $^3\sigma\pi^*$ state of Ru(SnPh₃)₂(CO)₂(iPr-DAB) is a bound state. Because of the delocalised character of the HOMO and LUMO, it is also expected to be only weakly distorted with respect to the ground state. This is in fact the case since the nanosecond TRIR spectra of this complex measured in a glass at 80 K showed only very small differences between the wavenumbers of the CO-stretching vibrations of the complex in its ground and $^3\sigma\pi^*$ state (Fig.4, right) (ref.14). The corresponding spectrum of Ru(Cl)(SnPh₃)(CO)₂(iPr-DAB) shows a shift of the v(CO) vibrations to higher frequencies by 18 and 29 cm⁻¹, respectively (Fig.4, left), which is characteristic of complexes having a lowest excited state with (partial) ^{3}MLCT character. The weak distortion was also evident from the emisson data (ref.21). Table I shows the emission properties for three representative complexes at 80 K. The excited state of Ru(Cl)(Me)(CO)₂(iPr-DAB) has mainly ^{3}MLCT character, a large apparent Stokes shift and a high value of

TABLE 1. Emission properties of three representative Ru(E)(E')(CO)₂(iPr-DAB) complexes in
a 2-MeTHF glass (80K, λ_{exc} = 460 nm).

| compound | | λ_{abs} | λ_{em} | Stokes shift[a] | τ | ϕ_r | k_r | k_{nr} |
E	E'	(nm)	(nm)	ΔE(cm⁻¹)	(μs)	(x10⁻⁴)	(s⁻¹)	(x10⁴s⁻¹)
Cl	Me	387	650	10455	0.3	3.4	1140	384.4
Me	SnPh₃	501	715	5974	31	10	32	3.19
SnPh₃	SnPh₃	495	670	5277	264	146	55	0.37

[a]apparent Stokes shift defined as E_{abs}-E_{em}

k_{nr}, which result in a rather short lifetime. For Ru(Me)(SnPh₃)(CO)₂(iPr-DAB) the lowest excited state has $^3\sigma\pi^*$ character and the complex is only weakly distorted in this state as can be seen from the much smaller Stokes shift and k_{nr} value and the much longer lifetime. An extreme situation occurs for the complex Ru(SnPh₃)₂(CO)₂(iPr-DAB) for which the delocalisation of the σ orbital results in a very small Stokes shift and k_{nr} value and in a lifetime of 264 μs, which is extremely long for a charge transfer state.

CONCLUSIONS

The above results clearly show that the dominant deactivation pathway of a $3\sigma\pi^*$ state is a chemical reaction (metal-ligand or metal-metal bond homolysis), instead of the ususal nonradiative decay to the ground state. Hence, the $^3\sigma\pi^*$ state may vary from very reactive and short lived to long lived and stable when the σ bond is strong and delocalised. Because of their high photoreactivity the metal-alkyl complexes may be good visible-light photoinitiators of polymerisation reactions. Further delocalisation of the σ–orbital over more metal centres e.g. by using high-nuclearity clusters, may lead to the development of a new class luminophores and/or photosensitizers.

ACKNOWLEDGEMENTS

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