Sigma-Bond-to-Ligand Charge Transfer Transitions and Excited States of d6 Metal-Diimine Complexes.
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SUMMARY

This thesis deals with the electronic transitions and excited state properties of a number of d^6 metal-metal and metal-alkyl bonded organo-transition metal complexes. In the introductory chapter 1, the important scientific aims and approaches of this PhD project were formulated. The exceptional photochemical and photophysical behaviour of these complexes is a consequence of the fact that their lowest-energy excited state has Sigma-Bond-to-Ligand Charge Transfer (SBLCT) character. Such SBLCT transitions transfer electron density from a σ-bonding orbital to an empty ligand orbital. As was outlined in section 1.3, this has two main consequences for the properties of the excited state reached after such an SBLCT transition. On one hand, the diminished electron density in the σ-bonding orbital causes a weakening of the corresponding bond. This leads to photochemical bond homolysis which can be extremely efficient. On the other hand, the SBLCT state has a very long lifetime whenever bond homolysis is not efficient. Such inefficient bond homolysis can be due to strong metal-ligand bonds or because the temperature is too low to allow thermally activated chemical reactions from the excited state.

The first aim of this PhD project was to obtain experimental evidence for the SBLCT character of low-lying allowed electronic transitions. The chosen experimental method was resonance Raman (rR) spectroscopy. From rR spectra it can be deduced which vibrations are affected by certain allowed electronic transitions and hence information can be obtained about the character of these transitions. For example, the rR spectra, obtained in chapter 3 by excitation into the MLCT transition of [Ru(Cl)(Me)(CO)_2(iPr-DAB)] and the SBLCT transition of [M(SnPh_3)_2(CO)_2(iPr-DAB)] (M = Ru, Os), are totally different. The former spectrum shows that symmetric CO- and CN-stretching vibrations, as well as the Ru–CO deformation vibration, are influenced by the MLCT transition. The latter spectrum shows the absence of ν_d(CO), but the presence of many in-plane and out-of-plane ligand and metal-ligand deformation modes. All these vibrations were assigned partly by means of DFT vibrational calculations. However, as chapter 8 shows, these differences can all be rationalized in terms of increase in metal-ligand interaction going from the first to the second type of complexes rather than ascribed to a difference in character of the electronic transition. Hence, for these complexes rR spectroscopy is not a suitable tool to determine the electronic
transition character. On the other hand, rR spectroscopy proved to be excellently suited to establish the SBLCT contribution to the electronic transitions of metal–methyl bonded complexes (chapters 7 and 8). To this end the Raman band due to the symmetric methyl deformation vibration was used. In rR spectra, obtained by excitation into MLCT transitions of e.g. [Ru(Cl)(Me)(CO)$_2$(iPr-DAB)] or [Re(Me)(CO)$_3$(iPr–DAB)], this band was hardly discernible, whereas it was the strongest band in the rR spectrum of e.g. [Pt(Me)$_4$(iPr-DAB)] where the electronic transition has SBLCT character. The conclusion of the experimental results described in chapter 8 is that resonance Raman spectroscopy can be an excellent tool to obtain experimental evidence for the character of electronic transitions, though certainly not for all systems.

A second question was whether complexes with a lowest $^3$SBLCT state can be made photostable. The most photostable complex known up to recently was [Re(SnPh$_3$)$_3$(CO)$_3$(dmb)], which still photodecomposes, however, from its $^3$SBLCT state with a quantum yield of 0.03–0.06 depending on the wavelength of excitation. From the complexes described in this thesis [Ru(SnPh$_3$)$_2$(CO)$_2$(pAn–DAB)], [Ru(SnPh$_3$)$_2$(CO)$_2$(pAn–BIAN)], [Os(SnPh$_3$)$_2$(CO)$_2$(iPr–DAB)] and [Os(SnPh$_3$)$_2$(CO)$_2$(dmb)] proved to be significantly more photostable (chapter 3). For the Ru complexes this was due to a lowering of the SBLCT state energy since the α-diimine ligand used had a very low-lying $\pi^*$ orbital. This increases the energy barrier for the thermally activated reaction from the relaxed excited state. For the Os complexes, it is the inherently strong Os–Sn bond that decreases the efficiency of the photochemical bond homolysis. An important consequence of the decrease of photolability was that the room temperature excited state lifetime is significantly enhanced (up to 3.6 μs in the case of [Ru(SnPh$_3$)$_2$(CO)$_2$(pAn–BIAN)]). The low excited-state energy of the Ru-complexes is an additional advantage in view of potential application as near-IR emitting labels (chapter 3).

Although these room temperature data already indicate that, despite their reactivity, SBLCT states may be much longer lived than MLCT states, this difference proved to be much more pronounced in low-temperature glasses, where homolysis reactions do not restrict the excited state lifetime. Mainly due to a much smaller distortion in the excited state, leading to a diminished vibrational overlap between ground- and excited states, SBLCT states proved to be much longer lived than MLCT states of related complexes. The longest emission lifetime, viz. 1.1 ms, was obtained for [Ru(SnPh$_3$)$_2$(CO)$_2$(dmb)] in 2-MeTHF at 90 K (chapter 3).

Interestingly, substituting Ru by Os in [Ru(SnPh$_3$)$_2$(CO)$_2$(dmb)] led to a fivefold decrease in excited state lifetime (chapter 3), while the absorption and emission energies
remained unaffected. In this way the influences of spin–orbit coupling on the excited state lifetime may be studied separately from those of excited state distortion and energy. Substitution of Ru and Os in the complexes \([M(SnPh_3)_2(CO)_2(iPr-DAB)]\) (\(M = Ru, Os\)) (chapter 3) for Pt (chapter 7) red-shifted absorption and emission energies of the resulting \([Pt(SnPh_3)_2(Me)_2(iPr-DAB)]\) complex due to decrease of frontier orbital delocalization, which decreases overlap stabilization and hence the HOMO-LUMO gap.

Chapters 3 and 4 describe the attempts to shift absorption and emission energies towards the red or near infrared (NIR) regions of the spectrum. The approach used in chapter 3 is to lower the LUMO energy, while in the experiments of chapter 4 the HOMO energy is raised. Both approaches result in complexes that emit in the NIR at 90 K, e.g. \(\lambda_{em} = 821\) nm for \([Ru(SnPh_3)(CO)_2(pAn–BIAN)]\) (chapter 3) and \(\lambda_{em} = 855\) nm for \([Ru{RuCp(CO)}_2_2(CO)_2(iPr-DAB)]\) (chapter 4). Interestingly, the use of the electron donating RuCp(CO)\(_2\) ligands in the latter complex stabilizes also the one-electron oxidized product, making this complex the only representative of this series for which such an oxidized species was ever observed. However, this approach where the σ–orbital energy is increased, suffers from the disadvantage that the resulting complexes are very photolabile at room temperature. Although (weakly) NIR-emitting complexes were obtained by both approaches, all these data were obtained from measurements on glassy solid samples at low temperature. At room temperature, no emission was observed from these complexes, while the emission of similar complexes emitting at higher energies was rather weak. The reason for the low emission quantum yield even at low temperature is not yet clear, but in view of the results of recent \textit{ab initio} calculations on the ground and excited states of the model complex \([Ru(SnH_3)_2(CO)_2(Me–DAB)]\) it is proposed that intersystem crossing from the optically populated \(^1\)SBLCT state to the emitting \(^3\)SBLCT state is inefficient due to the large energy gap between these states and because of competing nonradiative decay to another (non-emitting) triplet excited state (of \(^3\)MLCT character). One consequence is that future applications of these complexes as luminophores are rather improbable.

The other main property of SBLCT states, their efficient photoinduced radical formation, was successfully applied in the past since several d\(^6\) metal–alkyl complexes proved to be efficient photoinitiators for radical polymerizations. Chapter 5 reports the results of a more fundamental study of these radicals, viz. an FT-EPR study of the methyl radicals, obtained by irradiation of solutions of \([Pt(CH_3)_4(iPr–DAB)]\) and \([Ru(R)(SnPh_3)(CO)_2(iPr–DAB)]\) (\(R = CH_3, CD_3\)). This study confirms the triplet character of the excited state from
which the radicals are formed. By extensive variation of the solvent, the chemically induced
dynamic electron polarization (CIDEP) was shown to stem from combined contributions of
the ST₀ and ST₁ radical pair mechanisms. The absence of triplet mechanism induced CIDEP
in the radicals produced by irradiation into the lowest-energy absorption band suggests that
the radical formation is a very fast process. Very interestingly, the CIDEP pattern of the
photogenerated radicals is strongly excitation wavelength dependent. This rare observation
proves that radical formation proceeds according to different pathways depending on the
excitation wavelength.

Chapter 6 presents two novel complexes, [Rh(R)₂(I)(CO)(dmb)] (R = Me, iPr). The
structure of the methyl complex was solved by single-crystal X-ray diffraction. It was found
that excitation into the lowest absorption band of these complexes in solution gave rise to
homolytic Rh–R bond splitting. This photoreaction occurs after crossing from the optically
excited XLCT (X = I) to the reactive SBLCT state. For the iPr-complex homolysis is
observed at longer wavelength irradiation than for the methyl derivative, indicating that in the
former case the SBLCT-state is lower in energy.

It is clear from the foregoing that much more is known now about SBLCT states and
transitions in d⁶ metal–diimine complexes than when this PhD project started. The remaining
question is along which lines research of SBLCT states and transitions should continue and
what problems are still to be solved.

Important aspects of these complexes are their photolability and emission properties.
By varying the α-diimine ligand it was possible to make the complexes virtually photostable,
while at the same time lowering the SBLCT state energy to such an extent that emission in the
NIR was observed. Unfortunately, this emission was rather weak in a low-temperature glass
and not observable at room temperature. Although theoretical data give some clues about the
reasons for this behaviour, not found for complexes having a lowest MLCT state, further
research should first of all be concerned with this problem. This can be done by gaining
information from ultrafast time-resolved absorption studies, about the non-radiative decay
channels that decrease the emission efficiency of these complexes. The results of these studies
might indicate how such complexes with a lowest SBLCT state should be remodelled in order
to be not only photostable and possess very long emission lifetimes but also emit with high
quantum yields. Such time-resolved measurements may also indicate which factors determine
the shape of the potential energy curves of the SBLCT-states and the activation barrier for
dissociation in case of the photoreactive complexes.

Recently, ultrafast electronic absorption and time-resolved FT-EPR spectroscopic
measurements on metal–alkyl bonded complexes suggested that fast bond homolysis can occur from the Franck-Condon state. In contrast to these compounds, for many complexes described in this thesis, the SBLCT excited state has a well developed minimum in the potential energy surface. Further (ultrafast) time-resolved spectroscopic (UV/Vis, IR, FT-EPR) studies should be able to shed light on the excited state dynamics of such systems.

Apart from developing new systems that emit more strongly from their SBLCT states, it is of interest in any case to know which other complexes are characterized by a lowest SBLCT state. From the many studies that have already been performed, all, apart from those of the Os clusters [Os₃(CO)₁₀(α-diiimine)], dealt with d⁶ Mn, Re, Ru, Os or Pt complexes with α-diiimine ligands. It can be expected that lowest SBLCT states and transitions are not limited to these complexes. One striking absentee are the complexes of group 9 transition metal atoms. Although two rhodium–alkyl complexes were reported in chapter 6, where the occurrence of an SBLCT state was proven, the lowest-energy allowed transition has Halide-to-Ligand Charge Transfer rather than SBLCT character for these complexes. SBLCT systems should also not be limited to α-diiimine systems. Many other ligands are known with low-lying empty orbitals such as porphyrins.

Finally, the radicals formed by the homolysis reactions from the metal–diimine complexes with two σ-bonded ligands, described in this thesis, diffuse apart from each other, making the photoreactions irreversible. In the abovementioned Os clusters, the radicals are kept together in a biradical species by an Os(CO)₄ fragment, which can lead to interesting secondary reactions. Systems might be devised where the σ-bonded ligand is connected to the π-accepting ligand or to a co-ligand, which may give rise to similar biradical formation and interesting follow-up reactions.