Sigma-Bond-to-Ligand Charge Transfer Transitions and Excited States of d6 Metal-Diimine Complexes.
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Sigma-Bond-to-Ligand Charge Transfer Transitions and Excited States of d^6 Metal-Diimine Complexes

Efficient Radical Formation and Very Long-Lived Excited States

Joris van Slageren
Sigma-Bond-to-Ligand Charge Transfer
Transitions and Excited States of $d^6$ Metal–Diimine Complexes

Efficient Radical Formation and
Very Long-Lived Excited States

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Introduction:

*Excited States in Organometallic Chemistry*
1.1 A General Introduction

Over the past years an increasing amount of effort and creativity has been directed towards the justification of academic research. Since a scientist's mind is on the average endowed with an ample amount of imaginative powers, this has led to visions of future worlds in which mankind is surrounded by molecules and molecular materials performing all sorts of useful functions. In contrast, the research described in this thesis is more fundamental in character and deals with the interaction of light and certain organometallic complexes. It aims at understanding certain electronic transitions and subsequent excited state processes. This certainly does not exclude the possibility of application of the type of complexes described.

In the following section the process of light absorption as well as radiative and non-radiative excited state processes are briefly outlined. Many of the concepts described are implicitly or explicitly used in the experimental chapters of this thesis.

1.2 Absorption of Light and Excited State Processes\(^1-^3\)

Absorption of Light

The absorption of light can be considered to be a resonance phenomenon in which the electric field of light causes oscillation of the electrons in the molecule. Due to the quantized nature of electronic states only photons with an energy exactly corresponding to the energy difference between two electronic states may be absorbed. The probability that the interaction of light with the molecule indeed induces electronic excitation is given by the so-called oscillator strength, which is related to the experimental extinction coefficient. The oscillator strength is related to the square of the transition dipole moment, which is in turn governed by a number of selection rules, that can be divided into electronic, vibrational and spin factors. Thus, the transition moment is largest for transitions between orbitals that have good spatial overlap. Since light does not directly affect the electron spin, transitions during which the spin multiplicity remains the same (spin-allowed transitions) generally have transition dipole moments many orders of magnitude larger than spin-forbidden transitions. The transition dipole moment vector has the same group theoretical symmetry properties as the translations along the three Cartesian axes. Hence, from group theory one can deduce that the product of
the symmetry representations of the final wavefunction, one of the components of the transition dipole vector, and the initial wavefunction must be totally symmetric to yield a non-zero transition dipole moment. This leads for instance to the Laporte forbiddenness of ligand-field transitions in octahedral and other centrosymmetric complexes. However, vibrations and distortions may lift these symmetry restrictions. Furthermore, a certain amount of another transition may be admixed to the transition under study, which thus 'borrows' intensity.

![Diagram](image)

**Figure 1.1** A Jablonski diagram indicating radiative and non-radiative transitions between singlet (S) and triplet (T) states.

After absorption of a photon, a molecule finds itself in the excited state (in the following, by excited state generally *electronically* excited state will be meant). All molecules described in this thesis have a closed-shell ground state electronic configuration. This means that there are no unpaired electrons and the ground state has singlet spin multiplicity. In the excited state, the two unpaired electrons may have the same or opposite spin quantum numbers, which gives rise to triplet and singlet spin multiplicity of this state, respectively. For the same electronic state the singlet and triplet spin levels are separated by twice the amount of energy associated with electron repulsion due to electron exchange. Since the movement of
nuclei is slow compared to electron movement, the atoms are still at their ground state positions directly after arrival in the excited state (the Franck-Condon principle). Since the equilibrium positions of the atoms are different from those in the ground state, the molecule possesses excess vibrational energy at this point. By collisions with other molecules, the molecules can lose this energy. This process, which is called vibrational relaxation, is usually fast, e.g. in solution, but can be slow in the gas phase at low pressure. From the thermally relaxed excited state, non-radiative transitions can occur to other states during which the spin multiplicity is retained (internal conversion) or changed (intersystem crossing). Additionally, the energy corresponding to the loss of potential energy due to a transition can be emitted as a photon. These radiative and non-radiative transitions are discussed in separate sections below. Figure 1.1 depicts a very simple schematic picture of the possible transitions in a molecule (the Jablonski diagram).

**Non-radiative transitions**

Many radiationless transitions can be viewed as a jump from one potential energy surface to another at a certain molecular geometry, the crossing point (Figure 1.2). The electronic energy of the higher excited state is converted into vibrational and electronic energy of the lower excited state. In order for the radiationless transition at the crossing point to be allowed, it is essential that the two states are mixed to some extent at that point, creating an avoided crossing (Figure 1.2B and 1.2 C). However, if this mixing is very strong, the energy difference between the two potential energy surfaces is very large (Figure 1.2C) and no jump will occur. In this case the molecule remains on the same potential energy surface and only the state changes character.

![Figure 1.2 Depiction of adiabatic potential energy surface crossings with (A) no interaction between states, (B) weak interaction between the states and (C) strong interaction between the states.](image)

A number of different mechanisms may cause mixing of the two states concerned. Of these, vibrations are very important for internal conversion and non-radiative decay to the
ground state. Suitable vibrations, the so-called promotor vibrations, may cause the molecule to approach the crossing point geometry. Secondly, since energy must be conserved, after the non-radiative transition, the molecule is in a vibrationally excited state. The vibrations that have taken up this energy are called acceptor vibrations.

![Figure 1.3](image)

**Figure 1.3** Ground- and excited-state potential energy diagrams in (A) the reference situation, (B) a situation in which the excited state is severely distorted and (C) a situation with a small energy gap (E₀) between ground and excited states.

However, even if no crossing occurs between two surfaces, a jump from one to the other may occur. In this case the rate depends on the Franck-Condon factor, the amount of overlap between the iso-energetic vibrational wavefunctions of the two states. The magnitude of this vibronic overlap depends on the relative equilibrium nuclear displacement (ΔQₑ) and the energy gap (Figure 1.3). Figure 1.3A depicts a situation where the energy gap between ground and excited states is large and the distortion in the excited state small. In this case, the vibrational overlap is small, since the amplitude of the vibrational wavefunction of the ground state is small. In Figure 1.3B, the potential energy diagram is shown for a molecule which is severely distorted in the excited state. Since the amplitude of the ground state vibrational wavefunction is largest near the edges of the potential energy surface, the vibrational overlap is larger in this case. The same effect is observed for a decrease in energy gap between ground and excited states at constant nuclear displacement ΔQₑ (Figure 1.3C). Hence the slowest non-radiative decay rates (kₑ) can be expected for only slightly distorted excited states, with a large energy gap between ground and excited states. From theory, one can expect a linear relationship between \(\ln (kₑ)\) and the energy gap, if the excited state displacement is small.\(^4\)

This so-called energy gap law (EGL) has proven to give a successful description of non-radiative excited state decay in several series of transition metal complexes.\(^5\)\(^-\)\(^7\) Besides,
delocalisation of orbitals over more atoms causes a decrease in the average distortion of the bonds, leading to decreased displacement of potential energy curves along any normal coordinate. In a number of studies on coordination compounds this has proven to slow down the non-radiative decay process. These phenomena are of great importance for the work described in this thesis.

![Figure 1.4](image-url)

**Figure 1.4** Possible orientations of the electron spin magnetic moment vector with respect to a magnetic field, resulting in singlet and triplet states.

Vibronic interaction cannot directly change the spin multiplicity of an electronic state. Hence, for intersystem crossing processes another mixing mechanism is needed. In molecules with a closed-shell ground state, this is usually spin–orbit coupling. In a magnetic field, the magnetic moment due to a spinning electron may be represented by a vector precessing about the axis of this magnetic field. Since an electron can assume two different orientations with respect to this axis, the two unpaired spins of an electronically excited state can be parallel or anti-parallel, resulting in triplet and singlet excited states, respectively. Figure 1.4 depicts the possible relative orientations of the magnetic moment vectors with respect to each other. The strongest field present in a molecule, in the absence of an external magnetic field, is that created by the orbital motion of electrons. This results in three triplet sublevels (T₁, T₂ and T₃) that are not degenerate but separated by zero-field splitting. If one electron experiences a different magnetic field from the other, this will result in a difference in precession speed. Thus, from the pure singlet (S) state, the T₀ component of the triplet state is obtained (in the absence of an external field the triplet components are usually denoted T₁, T₂ and T₃). Alternatively, the spin vector may also flip from one orientation to the other. Due to the need for conservation of total angular momentum, the orbital angular momentum has to change simultaneously. This is made possible by spin–orbit coupling (SOC), the interaction of spin and orbital angular momenta. The magnitude of the spin–orbit coupling constant depends on
the principal and orbital angular momentum quantum numbers, but more importantly it increases with the fourth power of the nuclear charge. This is the basis of the so-called 'heavy atom effect'. Thus, whereas the SOC constant is negligible for H, it can be of the order of thousands of wavenumbers for heavy transition and main-group metal atoms.

However, the intersystem crossing rate between two states of different spin multiplicity is not only dependent on the magnitude of the SOC constant. First of all, since the spin–orbit coupling Hamiltonian has the same symmetry properties as the three rotations, the symmetry allowedness of intersystem crossing depends on the orbital symmetries of initial and final states and the symmetry point group of the molecule. This means that the three triplet sublevels (T_x, T_y and T_z) can be populated at different rates. However, spin–lattice relaxation is expected to cause a decay to equilibrium on a nanosecond timescale at room temperature. Secondly, the same factors influencing non-radiative transitions in general are of influence on the intersystem crossing rate (k_{ISC}). Thus, k_{ISC} increases with decreasing energy gap between the two states and with increasing vibrational overlap.

**Radiative transitions**

In principle, radiative transitions (luminescence) can be divided into spin-allowed (fluorescence) and spin-forbidden (phosphorescence). In molecules containing heavy atoms, such as the transition metal complexes described in this thesis, the spin character of electronically excited states is not pure, due to spin–orbit coupling. The radiative decay of such compounds is usually referred to by the general term luminescence. The efficiencies of radiative decay processes depend on a number of factors. Firstly, they depend on competing non-radiative decay rates. This leads for instance to the observation that luminescence usually occurs from the lowest excited state of given multiplicity (Kasha's rule), since the energy gap between the first and higher excited states is small, giving rise to efficient internal conversion to the lowest excited state. In addition, fluorescence efficiency depends on the depopulation rate of the excited singlet state by intersystem crossing. In the absence of non-radiative processes, the radiative rate constant is proportional to the absorption oscillator strength and the square of the absorption energy. Although theoretically only valid for atomic transitions, this was shown to be a good approximation for strongly allowed transitions in aromatic molecules. In general, radiative (k_{r}) and non-radiative decay (k_{nr}) rates can be separated experimentally by use of the observable quantities of luminescence lifetime (τ) and luminescence quantum yield (ϕ) according to equations 1.1 and 1.2:
Chapter 1. Introduction: Excited States in Organometallic Complexes

\[ k_r = \frac{\phi}{\tau} \quad (1.1) \]
\[ k_m = 1 / (\tau - k_r) \quad (1.2) \]

Equations 1.1 and 1.2 are only correct if the emitting state is the same as the optically excited state, or populated from the optically excited one with unity efficiency, and the only processes deactivating the excited state are non-radiative and radiative decay. This latter assumption is invalid if chemical reactions occur from the excited state. The former one is invalid if the optically occupied excited state radiatively or non-radiatively decays to the ground state, before crossing to the emitting state occurs. This is the case, for instance, when intersystem crossing from the singlet to the emitting triplet state is rather slow.

From Figure 1.3, it can also be deduced that the energy difference between absorption and emission increases with increasing distortion in the excited state. Conversely, experimental observation of this energy difference (the apparent Stokes shift) can serve as a measure for the distortion of complexes in the excited state.

One type of process has been neglected so far, and that is chemical reactions from the excited state. They may occur directly from the excited state if it is dissociative, i.e. if there is no minimum in the potential energy surface. Alternatively, non-radiative crossing from a non-dissociative to a dissociative excited state or thermal reactions from the excited state are possible pathways for photochemical reactions. As photochemical reactions are very important for the work described in this thesis, they are discussed below together with the general properties of different types of electronically excited states in organometallic complexes.

1.3 Types of Electronic Transitions and Excited States in Organometallic Complexes\textsuperscript{11-13}

In organotransition-metal complexes, molecular orbitals may or may not be situated on different parts (metal or ligands) of the molecule. Electronic transitions are classified according to the positions of the molecular orbitals involved (Figure 1.5). This section gives an overview and representative examples of different types of electronic transitions in transition metal complexes and the properties of the electronically excited states in which the complex may arrive due to these transitions. Obviously, in one particular complex different
types of electronic transitions and hence electronically excited states can occur. Which of these play a role, depends on the energy levels of metal and ligand orbitals and the interaction between them.

In this section only intramolecular excitations and excited state processes are treated. Bimolecular and supramolecular processes are out of the scope of this thesis, although such interesting phenomena as energy and electron transfer attract a lot of scientific attention nowadays.

The overview concludes with the particular type of electronic transition and excited state that the majority of this thesis deals with. Subsequently, in the final section of this chapter the aims and contents are given.

![Figure 1.5 Schematic overview of possible transitions in organometallic and coordination complexes.](image)

**Ligand Field (LF).**

These transitions, also known as d-d or metal-centered (MC) transitions are Laporte (symmetry) forbidden in centrosymmetric complexes, hence $\varepsilon$ (the molar extinction coefficient in M$^{-1}$cm$^{-1}$) is typically not higher than a few hundred. Since the splitting of the d levels of octahedral complexes is smaller for first than for second- and third-row transition metal atoms, the LF states often play a major role in the excited state behaviour of complexes of first-row transition metal atoms. Often LF excitation corresponds to a metal–ligand bonding to antibonding transition and hence leads to ligand dissociation. The photosubstitution of ligands by water in aqueous solution of Cr(III) complexes is a classical example. When thermally accessible from another type of excited state, LF states can play a role in the photochemistry of complexes where the lowest energy transition does not have LF character, like in the case of $[\text{Ru(bpy)}_3]^{2+}$. 
Intraligand (IL).

When one of the ligands possesses a low-lying electronic transition, this transition may also be lowest in energy in the complex. Intraligand or ligand centered (LC) excited states themselves are usually not reactive. Typical examples are some of the metalloporphyrins, as well as [M(bpy)_3]^{3+} (M = Rh, Ir).\(^{14}\) In this case the IL excited state properties (such as luminescence lifetime) are those of the free ligand, although modified by an external heavy atom effect. For example, the intersystem crossing efficiency of a zinc porphyrin system was greatly enhanced by peripheral introduction of ruthenium porphyrin units.\(^{15}\)

Metal-to-Ligand Charge Transfer (MLCT).

This type of electronic transition is the first we encounter in which actually both metal and ligand are involved. In this case, an electron is transferred from a metal d orbital to a low-lying empty orbital on a ligand. The oscillator strength for this type of transition is normally large, with extinction coefficients in the order of \(10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}\). The low-lying empty orbital involved in such an MLCT transition is very often a \(\pi^*\) orbital of a bidentate chelating nitrogen ligand such as bipyridine or phenanthroline.

Absorption bands corresponding to MLCT transitions are often very solvatochromic \(i.e.\) their position depends on the solvent polarity.\(^{16}\) Usually, they shift to higher energy in more polar solvents.\(^{17}\)

The prototypical example of a transition metal complex with a lowest MLCT transition is [Ru(bpy)_3]^{2+} (bpy = 2,2'-bipyridine).\(^{11,14,18,19}\) The main interest in this molecule stems from the fact that in the excited state it can transfer an electron to another molecule, to another part of a supramolecular assembly or to a semiconductor film and is also able to transfer its excited state energy to other molecules or parts of molecules. Interestingly, it was shown recently that the lowest energy \(3^{\text{MLCT}}\) state of this molecule is formed within 300 fs at room temperature.\(^{20}\) This means that the processes of vibrational relaxation and intersystem crossing are very fast in this system.

Ligand-to-Metal Charge Transfer (LMCT).

If a highly oxidized transition metal, \(e.g.\) Mn(VII) (d^0), is bonded to a reducing ligand such as oxide or sulfide, low lying absorption bands due to LMCT transitions may be
observed. A very typical example is the intensely purple coloured \( \text{MnO}_4^- \) anion. For these inorganic compounds no transitions can originate from the metal, since no \( d \) electrons are present. Organometallic and coordination compounds may also display optically allowed LMCT transitions, e.g. \([\text{Pd(Cl)}_2(L_2)] \) (\( L_2 \) is e.g. COD or 2 PPh\(_3\)).\(^{21,22}\)

**Ligand-to-Ligand Charge Transfer (L'LCT).**

In any organometallic or coordination complex with both reducing and oxidizing ligands, excited states may occur in which charge is transferred from one ligand to the other. If donor and acceptor parts are located on different parts of the same ligand, the transition is said to have 'intraligand charge transfer' character.\(^{12,23}\)

The lowest-energy excited state of several Re(I)-based chromophore-quencher (C-Q) complexes has L'LCT character.\(^{24-26}\) Since the electronic interaction between donor and acceptor is weak, the optical L'LCT transition of these C-Q complexes has an extremely low extinction coefficient (e.g. \( \varepsilon = 2.4 \text{ M}^{-1}.\text{cm}^{-1} \) in the case of \([\text{Re(py-PTZ})(\text{CO})_3(\text{bpy})]^{+} \); py–PTZ = phenothiazine-functionalized pyridine). However, the L'LCT state can be populated indirectly, by optical \( \text{d}_\pi(\text{Re}) \rightarrow \pi^*(\text{bpy}) \) MLCT excitation followed by py–PTZ \( \rightarrow \) Re intramolecular electron transfer. The decay to the ground state is mainly non-radiative and the excited state properties must be studied by transient absorption spectroscopy, or indirectly by the effect on the MLCT excited state lifetime of the chromophore. If the donor ligand is sensitive to oxidation, photochemical ligand fragmentation may occur.\(^{27}\)

In systems with an optically allowed L'LCT transition, the metal atom functions as an anchor to keep both ligands in close proximity. One could consider these systems as metal-substituted organic donor–acceptor compounds. Examples of such systems are tetrahedral zinc(II) complexes bearing both a polypyridyl ligand such as bpy and a dithiolate or two thiolate ligands. Since the metal is light, intersystem crossing is ineffective and the lowest excited state can be extremely long-lived, up to milliseconds at low temperatures.\(^{28}\) Interestingly, in the case of \( \text{Zn(PhS)}_2(\text{phen}) \) (phen = 1,10-phenanthroline), L'LCT excitation leads to PhS\(^+\) radical formation,\(^{29}\) which could indicate \( \sigma \)-bonding character of the HOMO (see next part).

Replacement of Zn(II) by Pt(II) results in square planar complexes. Due to the good overlap of (di)thiolate and diimine orbitals the extinction coefficients of the highly solvatochromic L'LCT absorption bands are in the order of \((4-19) \times 10^3 \text{ M}^{-1}.\text{cm}^{-1}\). The complexes are often luminescent in solution at room temperature with lifetimes ranging from
several nanoseconds to a microsecond.\textsuperscript{30} Resonance Raman measurements confirmed the L’LCT character of the lowest energy allowed transition.\textsuperscript{31}

In the latter complexes, the metal orbitals may be involved in the lowest-energy transition and in the lowest excited state to some extent. This is also the case in the complexes [Re(X)(CO)$_3$(α-diimine)] and [Ru(X)(CH$_3$)(CO)$_2$(α-diimine)] (X = Cl, Br, I) for which a gradual change from MLCT to L’LCT (L’ = halide) was observed for the lowest-energy allowed transition and excited state.\textsuperscript{32-36} This type of L’LCT transition was also referred to as Halide-to-Ligand Charge Transfer (XLCT) transition.

**Sigma-Bond-to-Ligand Charge Transfer (SBLCT).**

This type of excited state plays a crucial role in the research discussed in this thesis. Therefore, its properties are discussed in more detail. It is a special type of L’LCT transition, which occurs if the orbital from which the electron density originates has Metal–Ligand σ-bonding character. Already forty years ago, it was found that the 395 nm absorption band of [Be(CH$_3$)$_3$(bpy)] must be due to a transition from σ(Be–C) to π*(bpy). In the 70s Wrighton and co-workers studied the [M(L)(CO)$_3$(α-diimine)] (M = Mn, Re; L = Mn[CO]$_5$, Re[CO]$_5$, SnMe$_3$, SnPh$_3$, GePh$_3$; α-diimine = bpy, phen, biquin) complexes.\textsuperscript{37-39} They assigned the lowest-energy absorption band to a σ(M–L) → π*(α-diimine) transition, which was at the time a new type of electronic transition for transition metal complexes. Their assignment was based on a number of observations. The dependence of the absorption maximum on the nature of the α-diimine ligand ruled out IL or LF transitions. Furthermore, a σ(M–L) → σ*(M–L) assignment was considered unrealistic for the same reason, as well as on account of the fact that the absorption maximum was found to be sensitive to solvent and temperature unlike other complexes for which a σ → σ* transition had been established. The difference in energy between the MLCT band of \textit{e.g.} [Re(Cl)(CO)$_3$(α-diimine)] and the lowest-energy absorption band of the mentioned M–L complexes as well as their photolability in room temperature solution, prompted them to exclude an MLCT assignment of this absorption band. Later this assignment was disputed, since the resonance Raman spectra, obtained by irradiation into the lowest-energy absorption of [M{M'(CO)$_5$}(CO)$_3$(α-diimine)]\textsuperscript{40,41} and [M(SnPh$_3$)(CO)$_3$(α-diimine)]\textsuperscript{42} (M, M’ = Mn, Re), did not give any evidence of the involvement of the metal–metal bond in the electronic transition. The absorption band was reassigned to one or more MLCT transitions and the observed photoreactivity was ascribed to population of a reactive state by crossing from the optically accessible MLCT state.
In later years, more complexes were described where the observation of photolability was ascribed to the involvement of such a $\sigma\pi^*$ state. One of the complexes showing this behaviour is $\text{fac-[Ir(III)(tris-(6-isopropyl-8-quinolyl)dimethylsilyl)]}$\textsuperscript{43} and the $\sigma(\text{Ir-Si})\pi^*$ state of this complex giving rise to the Ir–Si bond homolysis was then called for the first time a 'sigma-bond to ligand charge transfer' or 'SBLCT' state. This notation (used in this thesis) and the orbital-based indication $\sigma\pi^*$ are equivalent.

The controversy about the character of the lowest-energy transitions of these metal-metal bonded $[\text{M(L)(CO)}_3(\alpha\text{-diimine})]$ ($\text{M} = \text{Mn, Re}$) complexes as well as their interesting photochemical behaviour, has sparked extensive theoretical, spectroscopic and photochemical research by our group. This research was not restricted to the above mentioned metal–metal bonded complexes, but included the isostructural Re–alkyl compounds $[\text{Re(R)(CO)}_3(\alpha\text{-diimine})]$ ($\text{R} = \text{Me, Et, iPr, Bz}$). Later, the investigations were extended to Ru complexes, e.g. $[\text{Ru(I)(R)(CO)}_2(\alpha\text{-diimine})]$ ($\text{R} = \text{iPr, Bz}$) and $[\text{Ru(L}_1\text{)(L}_2\text{(CO)}_2(\alpha\text{-diimine})]}$ ($L_1$, $L_2 = \text{e.g. alkyl, SnPh}_3$, Mn[CO]$_5$). These investigations and those of others yielded a huge amount of data from which some general conclusions can be drawn about the occurrence and properties of SBLCT transitions and excited states. These are outlined in the following paragraphs. First, attention is paid to complexes having lowest allowed SBLCT transitions, not coinciding with MLCT transitions.

In main group organometallic compounds, the metal orbitals are not involved in low-energy MLCT transitions, which might coincide or mix with SBLCT transitions. For instance, the complex $[\text{Zn(CH}_3)_2(\text{tBu-DAB})]$ ($\text{tBu-DAB} = \text{N,N'-di-tert. butyl-1,4-diaza-1,3-butadiene}$) possesses an optically allowed $\sigma(\text{C–Zn–C})\rightarrow\pi^*(\text{DAB})$ (SBLCT) transition which was studied well both from an experimental and a theoretical viewpoint. Calculations showed that the lowest-energy transition ($\epsilon = 1.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ in diethyl ether)\textsuperscript{44} occurs from the HOMO which consists of the antisymmetric $\sigma(\text{Zn–C})$ combination, to the $\pi^*(\text{tBu–DAB})$ LUMO.\textsuperscript{45} The decrease in electron density due to the electronic transition gives rise to Zn–C bond homolysis.\textsuperscript{44}

There are, however, also transition metal complexes with lowest SBLCT transitions. This is first of all the case when the metal is in a high oxidation state. A representative example is $[\text{Pt(CH}_3)_4(\text{R–DAB})]$ ($\text{R} = \text{tBu, cHx}$). DFT calculations showed that indeed the HOMO has $\sigma(\text{C}_ax–\text{Pt–C}_ax)$ character, with a small metal contribution while the LUMO mainly consists of the $\pi^*(\text{R–DAB})$ orbital.\textsuperscript{46} This suggests that the lowest-energy optically allowed ($\epsilon = 1.0 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ in toluene) transition can be attributed to a $\sigma(\text{C}_ax–\text{Pt–C}_ax)\rightarrow\pi^*(\text{R–DAB})$
Chapter 1. Introduction: Excited States in Organometallic Complexes

SBLCT transition. Another type of complexes with a pure lowest SBLCT transition are the metal–metal and metal–alkyl bonded compounds \([\text{Ru}(L_1)(L_2)(\text{CO})_2(\alpha\text{-diimine})]\) \((L_1, L_2=\text{e.g. alkyl, SnPh}_3, \text{Mn[CO]}_3)\). The lowest-energy, strongly allowed \((\varepsilon \approx 5 \times 10^3 - 10 \times 10^3 \text{ M}^{-1}\text{cm}^{-1})\),\(^{47-49}\) transition has again SBLCT character. This follows from density functional (DFT) MO-calculations on the model complex \([\text{Ru}(\text{SnH}_3)_2(\text{CO})_2(\text{H-DAB})]\),\(^{50}\) which show that the HOMO, denoted as \(\sigma(\text{Sn-Ru-Sn})\), is delocalized and consists of contributions from the anti-symmetric combination of the Sn fragment \(\sigma\) orbitals Sn(sp\(^3\)-sp\(^3\)) (42%), and H–DAB(\(\pi^*\)) (27%) orbitals, but only 15% from the Ru(5p) orbital. According to the calculations, the LUMO of the model complex is also delocalized since it has contributions from H–DAB(\(\pi^*\)) (61%), Ru(4dyz) (11%) and Sn(sp\(^3\)-sp\(^3\)) (27%). Accordingly, the lowest-energy HOMO→LUMO transition has SBLCT character. Because of the strong \(\sigma–\pi^*\) interaction, this transition is less solvatochromic than \(\text{e.g.}\) the MLCT transition of the isostructural complex \([\text{Ru}(\text{Cl})(\text{Me})(\text{CO})_3(\text{iPr-DAB})]\).\(^{33}\)

For many other complexes containing a metal fragment or alkyl group with a high-lying \(\sigma\) orbital, the character of the lowest-energy transition is less clear. A very well-studied series of complexes in this respect are the already mentioned Re and Mn complexes \([\text{M}(L)(\text{CO})_3(\alpha\text{-diimine})]\) \((\text{M} = \text{Mn, Re}; \text{L} = \text{e.g. alkyl, SnPh}_3, \text{Re}[\text{CO}]_5)\). High level (CASSCF/MR-CCI) quantum chemical calculations on the model complexes \([\text{M}(\text{R})(\text{CO})_3(\text{H-DAB})]\) \((\text{M} = \text{Mn, R} = \text{H, Me, Et}; \text{M} = \text{Re, R} = \text{H})\) show that the lowest-energy allowed transition has virtually pure MLCT character for \([\text{Mn}(\text{H})(\text{CO})_3(\text{H-DAB})]\) but strongly mixed MLCT/SBLCT character for \([\text{Mn}(\text{R})(\text{CO})_3(\text{H-DAB})]\) \((\text{R} = \text{Me, Et})\).\(^{51,52}\) Substitution of Mn by Re in the model complex \([\text{M}(\text{H})(\text{CO})_3(\text{H-DAB})]\) \((\text{M} = \text{Mn, Re})\) also results in a change in character of the lowest-energy allowed transition from pure MLCT to mixed MLCT/SBLCT.\(^{51,52}\) However, resonance Raman (rR) spectra, often used to characterize electronic transitions, do not give any evidence for the SBLCT character of the lowest-energy absorption band of these complexes. Thus, in the case of \([\text{Re}(\text{CH}_3)(\text{CO})_3(\alpha\text{-diimine})]\), no resonance enhancement was found for \(\nu(\text{Re-CH}_3)\), although the band due to the methyl deformation vibration is weakly visible.\(^{53,54}\) Similarly, the rR spectra of the metal–metal bonded complexes do not show a rR effect for the metal–metal stretching vibration. This implies that both the \(\sigma(\text{Re-CH}_3)\rightarrow\pi^*(\alpha\text{-diimine})\) and \(\sigma(\text{M-M'})\rightarrow\pi^*(\alpha\text{-diimine})\) SBLCT transitions are not optically allowed and that the reactive SBLCT state can only be occupied via an MLCT state. That the MLCT state can be lower or higher in energy than the SBLCT state, follows from UV-photoelectron spectra that show that the \(\sigma(\text{Re-CH}_3)\) orbital of \([\text{Re}(\text{CH}_3)(\text{CO})_3(\text{iPr-DAB})]\) is
lower in energy than the $d_{x}(Re)$ orbitals, whereas $\sigma(M-M')$ of the metal–metal bonded complexes $[M(M'(CO)_{3})(CO)_{3}(\alpha$-diimine)] (M, M' = Mn, Re) is higher.

The lowest-energy transition character in the triangular cluster complexes $[Os_{3}(CO)_{6}(\alpha$-diimine)] is even less clear. Previously it was assigned to a $d_{x}(Os)\rightarrow\pi^{*}(\alpha$-diimine) (MLCT) transition. However, recent DFT calculations suggest that the lowest-energy transition has $\sigma(Os-Os)\rightarrow\pi^{*}(\alpha$-diimine) character for $\alpha$-diimine = bpy, but for $\alpha$-diimine = R–DAB it has very mixed character best described as $\sigma(Os-Os)\pi^{*}(\alpha$-diimine)$\rightarrow\sigma^{*}(Os-Os)\pi^{*}(\alpha$-diimine). The properties of the lowest excited states of these complexes, are quite reminiscent of those of an SBLCT state (vide infra).

The foregoing dealt with the properties of SBLCT transitions. In recent years a lot of information has been derived from (time-resolved) spectroscopic studies of the specific photochemical and photophysical properties of SBLCT states. These data are reviewed below.

Apart from the lowest electronic transition, the lowest-excited state of $[Re(CH_{3})(CO)_{3}(\alpha$-diimine)] has also only little SBLCT character and the excited state lifetime of $[Re(CH_{3})(CO)_{3}(dmb)]$ in 2-MeTHF at 80 K is 5.0 µs, only slightly longer than that of the MLCT state of $[Re(Cl)(CO)_{3}(bpy)]$ (2.7 µs). Furthermore, going from the ground to the excited state, the shifts of the ν(CO) frequencies are the same for the two complexes. These observations seem to be in contradiction with the observed photolability of the $[Re(CH_{3})(CO)_{3}(\alpha$-diimine)] complexes. It was shown for $[Re(CH_{3})(CO)_{3}(dmb)]$, however, that this is due to the presence of two parallel pathways from the optically excited $^1$MLCT Franck-Condon state. One is the direct crossing to the reactive $^3$SBLCT state within 400 fs, the other is relaxation to the $^3$MLCT state, from which a reaction is not possible anymore. This shows that the Franck-Condon state must in fact have weakly mixed $^1$MLCT/$^1$SBLCT character. A similar ultrafast bond homolysis process was found for methylcobalamin; irradiation of this compound in the near UV (400 nm) gave rise to a partitioning between prompt bond homolysis and the formation of an intermediate species described as a cob(III)alamin-CH$_{3}$ ion pair, which in turn partly dissociates into radicals. At longer irradiation wavelengths only the latter pathway is found.

If the alkyl group R in $[Re(R)(CO)_{3}(\alpha$-diimine)] is a slightly stronger $\sigma$ donor than Me (e.g. Et, iPr, Bz), the lowest excited state obtains $^3$SBLCT character, although this state can still only be occupied via the MLCT states. This low energy of the $^3$SBLCT state increases the quantum yield of the photochemical Re–C bond homolysis of $[Re(R)(CO)_{3}(iPr-DAB)]$ from
0.01 ($R = \text{Me}$) to 0.77 ($R = \text{Bz}$) and even 0.99 ($R = \text{Et}$). Time-resolved IR measurements showed that, contrary to the behaviour of $[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dm})]$, the excited state CO-stretching frequencies of $[\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})]$ in n-heptane are hardly different from those of the ground state. Recent FT-EPR measurements confirmed the triplet character of the reactive excited state of these complexes.\textsuperscript{63}

Another series of complexes, in which the SBLCT excited state is not optically accessible are $[\text{Ru}(\text{I})(\text{R})(\text{CO})_2(\alpha\text{-diimine})]$ ($R = \text{iPr, Bz}$). However, population of the reactive $^3$SBLCT state through crossing from the non-reactive $^1$XLT ($X = \text{I}$) gives again rise to alkyl radical formation. These radicals were characterized by (FT-)EPR spectroscopic measurements.\textsuperscript{63,64}

Direct SBLCT excitation of $[\text{Pt}(\text{CH}_3)_4(\alpha\text{-diimine})]$ gives rise to efficient photochemical Pt–CH$_3$ bond homolysis from the $^3$SBLCT state.\textsuperscript{46,65–68} The photochemical reaction, which proceeds with almost unit efficiency in chlorinated solvents, is followed by very unselective chemical reactions.\textsuperscript{46}

The photochemical behaviour of complexes with a lowest $^3$SBLCT state depends on the metal–ligand bond strength in several ways. Thus, upon irradiation of $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-DAB})]$ in room temperature solution, only the Ru–CH$_3$ bond is broken,\textsuperscript{69} whereas in the case of $[\text{Ru}([\text{Mn}(\text{CO})_5](\text{CH}_3))(\text{CO})_2(\text{iPr-DAB})]$ only Ru–Mn bond splitting is observed.\textsuperscript{70}

The sensitivity of the photochemical behaviour to the metal–ligand bond strengths is further evidenced by the observation that the room temperature excited state lifetime of $[\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr-DAB})]$ is less than 5 ns,\textsuperscript{69} due to efficient Ru–CH$_3$ bond homolysis, while that of $[\text{Ru}([\text{SnPh}_3]_2)(\text{CO})_2(\text{iPr-DAB})]$ is ca. 1 μs, due to the strong Ru–Sn bonds.\textsuperscript{48} Depending on the metal–ligand bond strength, the photochemical reaction can be virtually activationless as in the former case, or thermally activated as in the latter ($E_a = 1.5 \times 10^3$ cm$^{-1}$). In the latter case the photochemical quantum yield is still rather high due to the long excited state lifetime. The complex $[\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr-DAB})]$ behaves similarly; it is quite photoreactive ($\Phi = 0.77$), but its lifetime ($2.5 \times 10^2$ ns in toluene at room temperature) is much longer than that of the stable $^3$MLCT state of $[\text{Re}([\text{Me})(\text{CO})_3(\text{Bu-DAB})]$ (~0.5 ns in CH$_2$Cl$_2$).\textsuperscript{71,72}

Due to the presence of a third metal atom, bond homolysis is reversible in the case of the cluster complexes $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$. Irradiation causes Os–Os bond homolysis yielding biradical species with lifetimes up to 1 μs at room temperature depending on the $\alpha$-
Interestingly, apart from back reaction to the starting compound, intramolecular charge redistribution may occur in coordinating solvents, giving zwitterionic complexes \([\text{"Os(CO)₄-Os(CO)₄-Os(CO)₂(solvent)(α-diimine)"}]\) with lifetimes of up to minutes. Recent time-resolved IR spectroscopic measurements provided the first experimental evidence for the conversion from biradical into zwitterionic species.

Apart from efficient bond homolysis, long excited-state lifetimes appear to be a general feature of \(^3\)SBLC T states, provided this lifetime is not decreased by photochemical instability. Thus, the luminescence lifetimes of the \([\text{Re(L)}(\text{CO})₃(α-diimine)]]\) complexes in low temperature glasses (to prevent thermally activated photochemical reactions) are normally much longer (up to \(1.1 \times 10^2 \mu s\) for \([\text{Re(SnPh)}₃(\text{CO})₃(\text{dmb})]\)) than those of \(^3\)MLCT states. For the ruthenium complexes \([\text{Ru(L)}(\text{L}_2)(\text{CO})₂(α-diimine)]\) \((L_1, L_2 = \text{e.g. alkyl, SnPh₃, Mn[CO]}₃)\) the excited state lifetimes under similar conditions can be even longer (up to \(2.6 \times 10^2 \mu s\) for \([\text{Ru(SnPh)}₃(\text{CO})₂(\text{iPr-DAB})]\)). In some cases SBLC T states are reactive even in low temperature glasses. For instance, no luminescence was observed for \([\text{Pt(Me)}₄(bpy)]\).

It is clear from the foregoing that a lot is known about SBLC T states and transitions in \(d^6\) metal–diimine complexes. However, many questions remain, such as: How can we prove the SBLC T character of an electronic transition experimentally? Can the \(^3\)SBLC T state be made unreactive? How far can we extend the \(^3\)SBLC T state lifetime? What exactly is the influence of the central metal atom on the excited state properties and dynamics? How far towards the NIR can the excited state energy be tuned? Can we get more information about the radical formation process? Can we extend the series of complexes with low lying SBLC T states to other transition metals? The aim of this PhD project is to provide an answer to these questions.

### 1.4 Aims and Contents of this Thesis

This section outlines the approaches chosen to answer these questions in separate sections, followed by a brief overview of the contents of chapters 2 to 8.

In several chapters attention is paid to the experimental characterization of the electronic transitions by resonance Raman (rR) spectroscopy (chapter 3, 4, 6 and 7). The final chapter (chapter 8) gives a critical discussion of the influence of the electronic transition
character, metal–ligand interaction and orbital delocalization on the rR spectra. The experimental data from the preceding chapters as well as from literature are included for this purpose.

By increasing the metal–ligand bond strengths, the homolysis efficiency is expected to decrease, which can eventually yield photostable complexes with lowest SBLCT excited states. In chapter 3, the influence of replacing Ru by Os in \([M(SnPh_3)_2(CO)_2(\alpha\text{-diimine})]\) is investigated. This replacement can be expected to increase the M–Sn bond strength, since transition metals from the third period generally form stronger bonds than those from the second period. As in these \([M(SnPh_3)_2(CO)_2(\alpha\text{-diimine})]\) complexes the photochemical reaction is thermally activated, lowering the SBLCT excited state energy might increase the activation energy for crossing to the reactive excited state. To this end \(\alpha\)-diimine ligands with low-lying \(\pi^*\) orbitals are introduced, also in chapter 3.

In general, the excited state lifetimes of a series of complexes with similar characters of their lowest-excited states can be enhanced by increasing the rigidity of the complex (see chapter 1.2). This influence of rigidity is investigated in chapter 3, by comparing the excited state properties of the iPr-DAB \((N,N'\text{-disopropyl-1,4-diaza-1,3-butadiene})\) and the relatively rigid dmb \((4,4'\text{-dimethyl-2,2'-bipyridine})\) complexes. At room temperature, the excited state lifetime is expected to depend on the metal–ligand bond strength. Thus, by the same methodology of the preceding paragraph, it was attempted to increase the room temperature excited state lifetime.

Since the central metal atom is involved to a limited extent in the SBLCT transitions and excited states of the studied complexes, the question arises what influence this metal atom can exert on the excited state energy and lifetime. The results of this investigation are presented in chapter 3 for Ru and Os, and in chapter 7 for Pt.

The series of complexes with low lying SBLCT excited states is further extended to the \(\text{cis-[Rh(R)_2(I)(CO)(dmb)]}\) \((R = \text{Me, iPr})\) complexes of chapter 6.

The excited-state energy of SBLCT states depends to a first approximation on the energy of the \(\sigma\) orbital as well as on that of the ligand \(\pi^*\) orbital. Thus, by increasing the \(\sigma\) orbital energy (chapter 4) or decreasing the \(\pi^*\) orbital energy (chapter 3), the excited-state energy is expected to decrease, possibly giving rise to near infrared emitting complexes.

Apart from determining the efficiencies of photochemical bond homolyses (chapter 3 and 4), a large amount of information about the radical formation dynamics may be obtained from time resolved FT-EPR spectroscopic studies. Such an investigation and its results are
described in detail in chapter 5.

The contents of this thesis are as follows:

Chapter 2 discusses the experimental and theoretical research methods used in this thesis. The aim is to give short outlines of these methods, rather than comprehensive reviews for which the reader is referred to the literature.

Chapter 3 deals with the synthesis, electronic transitions and physical properties of the SBLCT excited states of a series of \([M(SnR_3)_2(CO)_2(\alpha\text{-diimine})]\) (\(M = \text{Ru, Os}; R = \text{Me, Ph}\)). The influence of \(M, R\) and the \(\alpha\text{-diimine ligand}\) are discussed mainly using resonance Raman as well as time-resolved absorption and emission spectroscopies at various temperatures.

Chapter 4 investigates the consequences of incorporation of electron rich \([\text{RuCp(CO)}_2]\) groups as axial ligands on the photochemical, photophysical and redox properties of \([\text{Ru}(L_1)(L_2)(CO)_2(\text{iPr–DAB})]\) (\(L_1, L_2 = \text{SnPh}_3, \text{RuCp[CO]}_2\)) at various temperatures.

Chapter 5 reports the results of a detailed time-resolved FT-EPR investigation of the photochemical methyl radical formation from \([\text{Ru(Me)(SnPh}_3(CO)}_2(\text{iPr–DAB})]\) and \([\text{Pt(Me)}_4(\text{iPr–DAB})]\). By variation of excitation wavelength and solvent viscosity, important information is obtained with regard to the spin character of the excited state and the dynamics of the radical formation process.

Chapter 6 extends the family of complexes having low-lying SBLCT excited states to the Rh complexes \(\text{cis-[Rh(R)}_2(I)(CO)(dmb)]\) (\(R = \text{Me, iPr}\)). In this chapter the synthesis, structure and photochemical homolysis reactions of these complexes are discussed.

Chapter 7 studies the ground state electronic structures and SBLCT electronic transitions in \([\text{Pt}(I)(\text{Me)}_3(\text{iPr–DAB})], [\text{Pt}(\text{Me)}_4(\alpha\text{-diimine})]\) and \([\text{Pt}(\text{SnPh}_3)_2(\text{Me)}_2(\text{iPr–DAB})]\) using DFT calculations and resonance Raman spectroscopy. In addition, the low temperature emission properties and the influence of excited state character thereon are discussed.

Chapter 8 gives a critical assessment of the use of resonance Raman spectroscopy for the study of electronic structure and transitions in \(d^6\) metal–diimine complexes. The influences of electronic transition character, metal–ligand interaction and orbital delocalization are discussed.
Chapter 1. Introduction: Excited States in Organometallic Complexes

1.5 References

Chapter 1. Introduction: Excited States in Organometallic Complexes

Chapter 1. Introduction: Excited States in Organometallic Complexes


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CHAPTER 2

Research Methods and Backgrounds
2.1 Introduction

In this chapter the most important methods (experimental and theoretical) used for the research described in this thesis are discussed. Firstly, a number of (time-resolved) spectroscopic methods to investigate electronic transitions, the physical properties of the excited state and the product formation and dynamics of photoinduced chemical reactions are discussed. Subsequently, (spectro)electrochemical techniques are briefly introduced. The chapter closes with some information on the quantum chemical calculation methods used in this thesis.

2.2 (Time-Resolved) Spectroscopic Techniques

Traditionally, in order to investigate their mechanisms, photochemical reactions were studied at low temperatures. Apart from studies in conventional solvents, many experiments were performed in liquid xenon or in solid matrices.\(^1\)\(^-\)\(^3\) Lowering the temperature slows down or stops secondary (thermal) reactions, allowing the primary photochemical steps to be studied by steady-state spectroscopic techniques. The other approach is to use time-resolved techniques. This is the only option for studying excited states and processes that are very fast even at low temperatures. The various (time-resolved) spectroscopic techniques used in this thesis are outlined hereinafter.

2.2.1 Resonance Raman (rR) Spectroscopy.\(^4\)\(^-\)\(^6\)

If a sample is irradiated with light, most of the photons (if not absorbed or reflected) pass straight through. However, some photons are scattered, due to the dipole which is induced in the molecule by the fluctuating electric field of the light. This is the same phenomenon that is responsible for the blue colour of the sky. The Nobel prize winning observation was that some of the scattered light has a different wavelength from that of the incident light.\(^7\) It was shown that the energy difference is exactly one vibrational quantum. The situation in which the molecule is initially in the zeroth vibrational level of the ground state and ends up in the first excited vibrational level, is called Stokes Raman scattering. In the less common situation that the molecule is initially in the first vibrationally excited state,
we are dealing with anti-Stokes Raman scattering. Scattering can be considered as a two photon process, in which the molecule is taken from an initial to a final state through some intermediate, virtual state (Figure 2.1).

![Figure 2.1](image)

**Figure 2.1** Mechanisms of Rayleigh, Stokes Raman and anti-Stokes Raman scattering. $\nu$ is the frequency of the incident light and $\nu_i$ is the frequency of a certain vibration.

The intensity of the Raman-scattered light is proportional to the square of the polarizability, connected to the mobility of the electrons of the molecule. An interesting situation arises when the energy of the incident light approaches a strongly allowed electronic transition. In this case the polarizability is given by eq. 2.1:

$$\alpha_{\eta\eta} = \frac{1}{\hbar c} \langle e|\Psi_e|g\rangle^2 \sum_k \frac{\langle f|\nu_i\rangle\langle\nu_i|i\rangle}{\nu_e - \nu_{gi} - \nu_{exc} + i\Gamma_{ev}}$$

where $g$ and $e$ are the electronic ground and excited state, respectively; $i$, $\nu$ and $f$ are the vibrational wavefunctions of initial, virtual and final vibrational levels, and $\langle e|\Psi_e|g\rangle$ is the electronic transition dipole moment.

Inspection of eq. 2.1 immediately shows that in this situation, the difference between $\nu_e - \nu_{gi}$ (the frequency difference between a vibrational level of the excited state and the ground state) and $\nu_{exc}$ (the excitation frequency) becomes very small and hence the polarizability very large. In this case it is assumed that the states involved in the scattering process are only those that the excitation light is in resonance with. A number of other requirements for a large polarizability (and hence a large resonance enhanced Raman intensity) is immediately clear as well: as Raman scattering is a two-photon process, it depends on the square of the electronic transition dipole moment and resonance enhancement is therefore strongest for strongly allowed electronic transitions. Furthermore, since the molecule is normally in a totally symmetric ground state, both the virtual and final vibrational
levels need to be totally symmetric as well, in order for the two overlap integrals in eq. 2.1 to be non-zero. Hence, only bands due to totally symmetric vibrations are observed in rR spectra. These overlap integrals are largest if the ground and excited state potential energy curves are strongly displaced. Therefore, the magnitude of the resonance enhancement of the Raman intensity of a band due to a certain normal vibration increases with increasing distortion along that normal coordinate upon excitation. It is on these last two observations that much of the interpretation of rR spectra in this thesis is based (chapter 3, 4, 6, 7, 8).

Although outside of the scope of this thesis, from careful intensity analysis in combination with computational techniques such parameters as the excited state distortions and vibrational reorganization energies may be extracted.\textsuperscript{4,8,9}

As a light source in our laboratory an Ar\textsuperscript{+} laser is used in combination with Coherent model CR490 and CR590 dye lasers, employing Stilbene, Coumarin 6 and Rhodamine 6G dyes, giving an excitation range of 430 – 600 nm. Traditionally a very high quality monochromator in combination with a photomultiplier is used. However, in our laboratory the scattered light is detected by a CCD camera, decreasing recording times.

2.2.2 (Time-Resolved) Emission Spectroscopy

Continuous wave (CW) emission spectroscopy typically employs a mercury or xenon lamp as the excitation source. The desired excitation wavelength is selected by a monochromator. The emitted light is passed through a second monochromator, which is scanned through a certain wavelength range. The light is generally detected by a photomultiplier tube. In this way, the emission spectrum is obtained. Keeping the emission monochromator at a set wavelength and scanning the excitation monochromator yields the excitation spectrum. Usually, the luminescence quantum yield is obtained by measuring the integrated emission intensity of the sample and of a reference with known quantum yield under the same conditions, \textit{e.g.} \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) \(\phi_{em} = 0.062\) in deaerated CH\textsubscript{3}CN). Corrections must be made for the absorption at the excitation wavelength, the refractive index of the solvent according to:

\[
\phi_{em}^s = \phi_{em}^r \left( \frac{I_s}{I_r} \right) \left( \frac{A_r}{A_s} \right) \left( \frac{n_s}{n_r} \right)^2
\]  

(2.2)

where \(s\) is the sample, \(r\) is the reference, \(I\) is the integrated emission intensity, \(A\) is the absorption at the excitation wavelength and \(n\) is the refractive index of the solvent.
Apart from the luminescence quantum yield and emission maximum, the emission lifetime ($\tau$) is another important parameter. To determine this quantity, time-resolved methods are necessary. These employ pulsed lasers such as nitrogen or Nd:YAG lasers, if necessary in combination with suitable dye lasers. The emission can be measured at a single wavelength using a monochromator and a fast photomultiplier connected to an oscilloscope. Alternatively, a spectrographic detection system (a grating in combination with a diode array or CCD detector) can be used. The detector is 'switched on' for a certain time (the gating time) starting from an arbitrary delay after the laser pulse. This has the advantage that the spectrum is recorded in a single shot rather than point by point. The disadvantage is that for decay analysis the experiment has to be repeated at many different delays in order to make fitting to an exponential function sensible. In this PhD project, such an optical multichannel analysis (OMA) setup was used. The emission spectra were recorded using at least 30 different delay settings, spanning at least three lifetimes. For fitting to biexponential or higher order functions single line measurements should be used. The emission quantum yields, reported in this thesis, were obtained with the same setup as used for the time-resolved measurements. A very long gating time was used to ensure detection of all the emitted photons. Comparison to a reference compound (see eq. 2.2) gave the emission quantum yield. From the emission quantum yield ($\phi_{em}$) and the emission lifetime ($\tau$), the radiative ($k_r$) and non-radiative ($k_{nr}$) decay rate constants can be calculated according to equation (2.3 and 2.4):

$$k_r = \phi / \tau$$

$$k_{nr} = 1 / \tau - k_r$$

assuming that the emitting state is populated from the optically occupied one with an efficiency of unity (see section 1.2).

### 2.2.3 Time-Resolved Absorption Spectroscopy

Apart from determining the parameters for the radiative and non-radiative decay of the excited state, a great deal of information about the excited state can be obtained from its absorption spectrum. The first absorption spectrum of an excited state (of fluorescein in boric acid) was already obtained in 1941. Apart from excited states, transient absorption spectroscopy is also suitable for the study of short-lived photochemical intermediates. The
contemporary setup is similar to the time-resolved emission setup described in the previous section, with the exception that a second light beam is needed to record the actual absorption spectrum (the probe beam). In the nanosecond to microsecond time domain, this is usually a flash lamp. The pump and probe beams can be perpendicular (in this thesis) or nearly collinear. The monitoring light can be detected by a monochromator-photomultiplier combination or alternatively, (this thesis) by the OMA detection system described in the previous section. To correct for variations in the monitoring light intensity a reference monitoring beam is needed in the latter type of setup. Both monitoring beams are transferred via optical fibers to the CCD detector and their intensities are recorded at the same time. It is possible to direct both beams through the same cuvette, while exciting only one part, using e.g. 1.0 mm holes for the monitoring beams and a 1 cm slit for the pump beam. It was found in our laboratory that employing a 50% mirror to divide the monitoring light, sending one part through the excited sample and one part through a reference cuvette greatly improved the signal-to-noise ratio. This is due to variable inhomogeneity of the monitoring light spot. Using the 50% mirror, the same part of this spot is used for both sample and reference beams, thus eliminating that part of measurement noise. Figure 2.2 shows a schematic representation of the setup used.

![Schematic setup](image)

**Figure 2.2** Schematic setup for transient absorption measurements.

Since most of the complexes studied are photolabile to a certain extent, a flow-through system had to be employed. To this end the outer compartments of two (sample and reference) thermostatible cuvettes (Hellma 160.001-QS) were connected in series to a pump (Verder 2040). At least 30 mL of solution was circulated through this closed system.
2.2.4 Time-Resolved Infrared (TRIR) Spectroscopy\textsuperscript{12-15}

Most of the complexes described in this thesis bear carbonyl ligands. The frequencies of the stretching vibrations of carbonyl ligands (ν(CO)) are very sensitive to the electronic and molecular structure of the complex. Moreover, the extinction coefficients of absorptions due to these vibrations are high and the carbonyl stretching region of the infrared (IR) spectrum is relatively transparent. This makes IR-spectroscopy an excellent tool for investigating carbonyl complexes. Since excited states and primary photoproducts are often short lived, time resolved IR spectroscopy is a convenient means for their study.

Over the past decade TRIR spectroscopic techniques have evolved enormously. Many TRIR studies of transition metal complexes have been concerned with their MLCT excited states. It was shown that the carbonyl stretching vibrations normally shift to considerably higher frequencies going to an MLCT state, since lowering the electron density on the transition metal atom decreases the metal–CO π-backbonding. Much smaller shifts of the ν(CO) frequencies have been observed for the IL excited state of \([\text{Re}(\text{PPh}_3)(\text{CO})_3(\text{dppz})]^{+}\)\textsuperscript{16}, the L'LCT (L' = I) excited state of \([\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]\)\textsuperscript{17} and the SBLCT excited states of \([\text{Re}(\text{Bz})(\text{CO})_3(i\text{Pr-DAB})]\)\textsuperscript{18} and \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(i\text{Pr-DAB})]\).\textsuperscript{19} In these cases the metal is not or hardly involved in the electronic transition. The ν(CO) bands may then even shift to lower frequencies since the α-diimine ligand is a weaker π-acceptor in the excited state, compared to the ground state, increasing the metal–CO π-backbonding in the excited state.

Initially, TRIR spectra were recorded using tunable IR lasers and fast IR detectors. In the last few years, step-scan Fourier Transform IR has been increasingly used to this end.\textsuperscript{20} Recently, sub-picosecond time resolutions have been achieved by pump-probe methods similar to those used in ultrafast transient electronic absorption spectroscopy.\textsuperscript{12}

2.2.5 Electron Paramagnetic Resonance (EPR)\textsuperscript{21}

The essential requirement for a compound to be EPR active is the presence of one or more unpaired electrons. Apart from stable radicals, reactive radical species can be generated e.g. by (electro)chemical one-electron reduction or oxidation of a diamagnetic parent species, or by photoinduced chemical processes such as bond homolysis or electron transfer. Unstable radical species can be transformed into relatively stable radicals by reaction with e.g. nitroso compounds, that give stable radical adducts. This is called the spin-trapping technique.
EPR spectroscopy is based on the fact that the energies of the two electron spin levels are inequivalent in a magnetic field, separated by the so-called Zeeman splitting. When the molecule is irradiated with microwaves of an energy corresponding to the energy difference between the spin levels, absorption of radiation can occur. The resonance condition is:

\[ h\nu = g\mu_B B \]  

(2.5)

where \( B \) is the magnetic field, \( \mu_B \) is the Bohr magneton \((9.273 \times 10^{-24} \text{ JT}^{-1})\), and \( g \) is the \( g \) value, which is comparable to the chemical shift in NMR. This \( g \) value is 2.00226 for a free electron. The observed \( g \) value for a radical deviates from this value, if the applied magnetic field induces a local electric current. Nuclei with non-zero spin quantum numbers induce a local magnetic field at the position of the unpaired electron, due to their nuclear spin. Consequently, the resonance line is split into a number of lines corresponding to the number of possible spin orientations of the nucleus. This phenomenon is called hyperfine splitting. It is on this effect that much of the merit of the EPR technique is based, since the magnitude of this splitting effect, the hyperfine splitting constant, depends on the distance between the nucleus and the unpaired electron. Hence determination of the hyperfine splitting constants gives information about the electronic structure of the studied paramagnetic species.

Typically, commercial instruments use a klystron as microwave source, that operates at a set frequency, usually at ca. 10 GHz (the X-band of microwave radiation). The corresponding magnetic field (of ca. 0.3 T) is produced by an electromagnet. The EPR spectrum is recorded by Sweeping the magnetic field and observing the change in absorption of microwave radiation. To improve the signal-to-noise, the field is usually modulated (typically at a 100 kHz frequency) with an amplitude less than the resolution desired, due to which the EPR spectrum is obtained as its first derivative.

2.2.6 Fourier-Transform Electron Paramagnetic Resonance (FT-EPR)\textsuperscript{22-24} and Chemically Induced Dynamic Electron Polarization\textsuperscript{25,26}

The short lifetime of free radicals created a need for time-resolved methods in EPR spectroscopy as well. Whereas the lower intrinsic sensitivity of NMR compared to EPR, resulted in the development of Fourier Transform (FT) NMR techniques at an early date, this development has been relatively slow in EPR. As the principles are identical, they can be found in any FT-NMR textbook. Briefly, a short pulse of electromagnetic radiation causes 90° change of the magnetization direction from the z-axis (the direction of the external magnetic
field) to the xy-plane. The magnetization, which now rotates in the xy-plane, induces an alternating current in the receiver coil. With time the magnetization returns to the equilibrium direction and the signal fades. This free induction decay (FID) represents the spectrum of the paramagnetic species in the time domain. Fourier transformation yields the spectrum in the frequency domain (Figure 2.3).²³

![Image of free induction decay (FID) recording and Fourier transform]

**Figure 2.3** Example of free induction decay (FID) recorded after a 90° microwave pulse and the frequency domain spectrum of a radical obtained after Fourier transformation.

The actual FT-EPR spectrometer used has been described.²⁴,²⁷ The generated microwave radiation is amplified by a travelling wave tube amplifier (TWT), that generates 1 kW microwave pulses (of ca. 15 ns duration) which pass through a variable attenuator into the microwave cavity. The microwave signal generated by the sample is frequency down converted by mixing with a reference signal from the microwave source in a quadrature IF mixer. The two-channel output (corresponding to the FID of the magnetization along the x- and y-axes) is fed to a digital oscilloscope. A CYCLOPS phase cycling routine is used to correct for imperfect quadrature detection. Typically 100 FIDs per phase (400 in total) are averaged by the oscilloscope before transfer to the controlling computer. The phase of the output signal is slightly dispersive, which can be corrected for by using a stable radical
Chapter 2. Research Methods and Backgrounds

reference. The spectral bandwidth covered by a single microwave pulse is limited by inequality 2.6:

\[ |\omega_{res} - \omega_{mw}| < \gamma_e B_1 \]  

in which \( \omega_{res} \) and \( \omega_{mw} \) are the resonance and applied microwave frequencies, respectively, and \( \gamma_e \) is the gyromagnetic ratio of the electron spin and \( B_1 \) is the strength of the microwave field.

For the equipment used, this yields a bandwidth of 12 G. Hence, spectra covering more than this range must either be corrected for loss in intensity or obtained at several field settings. Another limitation of the equipment is that during the first 120 ns after the microwave pulse, no signal can be recorded due to cavity ring-down. In practice this limits the applicability of the technique to radicals with a line width of less than 1 G. By linear prediction singular value decomposition (LPSVD), which is based on the assumption that the FID can be represented as the sum of a number of exponentially damped sinusoids, the missing part of the FID can be reconstructed. This results in an increase of signal-to-noise, but can create artifacts in the frequency-domain spectrum.

In the studies described in this thesis the radicals were generated by a pulsed laser. By varying the delay between laser and microwave pulses, information about the radical kinetics can be obtained. Importantly, the FID represents the time-domain spectrum of the radicals present at the time of the microwave pulse. Any radical formation or decay during FID recording only causes line broadening in the frequency domain spectrum. An effect of the short time delay between radical formation and measurements is that the spin distribution may deviate from Boltzmann equilibrium values. The spin distribution will eventually decay to the Boltzmann equilibrium through spin–lattice relaxation (after several microseconds). Processes that create non-Boltzmann electron spin distributions are collectively known as chemically induced dynamic electron polarization (CIDEP) mechanisms. The mechanisms that are important in this thesis are outlined below. More mechanisms exist, notably those in which a (stable) radical interacts with a triplet excited state, but these are not discussed here.

**Hyperfine dependent CIDEP mechanisms**

**\( ST_0 \) Radical Pair Mechanism (\( ST_0 \) RPM)**

A photochemically generated geminate radical pair is created with singlet or triplet character depending on the spin multiplicity of the excited state which it originates from. The
energies of the two spin states of the radical pair are separated by twice the exchange interaction \((J)\). Since the singlet radical pair state is considered the bonding state, \(^{28}J\) is negative for neutral radical pairs. In the case of radical ion pairs indications for positive signs of \(J\) have been obtained.\(^{29}\) The exchange interaction is far too large for any efficient interaction to occur between the singlet and any of the triplet sublevels. However, if the radicals diffuse apart within the solvent cage, the exchange interaction, which depends on the overlap of the unpaired electron orbitals,\(^{28}\) rapidly decreases until the singlet (S) level and the \(T_0\) component of the triplet level are degenerate (Figure 2.4). At this point the hyperfine interaction may induce differences in precession frequencies of the two radicals and mixing between the S and \(T_0\) spin levels occurs. However, the magnetic hyperfine interaction itself cannot create spin polarization,\(^{30}\) whereas exchange interaction can. Hence a re-encounter of the two radicals in the solvent cage is needed. This process can be repeated, increasing the generated polarization. Thus the magnitude of the generated polarization depends on the time the radical pair spends in the solvent cage and hence it is expected to increase with increasing solvent viscosity. The sign of the polarization in one hyperfine component of the EPR spectrum depends on the sign of the exchange interaction and the spin multiplicity of the excited state precursor. This leads to the general observation that for a negative exchange energy and a triplet precursor, low field peaks are in emission and high field peaks are in absorption. The magnitude of the spin polarization of a certain hyperfine component depends on the difference in resonance frequencies between that hyperfine component and the hyperfine components of the other radical of the pair. Finally it must be noted that \(ST_0\) mixing does not create net spin polarization, but rather redistributes spins of the two radicals of the pair.

**ST\(_{-1}\) Radical Pair Mechanism (ST\(_{-1}\) RPM).**

It can be seen from Figure 2.4 that mixing between the S and \(T_{-1}\) levels is also possible. However, since the mixing region is small, it has been generally assumed that this type of RPM is only important for systems with large hyperfine interactions or in viscous solvents (in which the radicals are kept in close proximity for a long time).\(^{24,26}\) Due to the need for total angular momentum conservation, a hyperfine-interaction-induced nuclear spin flip has to occur simultaneously with the electron spin flip (in the opposite direction and on the same radical). If the radical pair is initially formed in the \(T_{-1}\) (\(\beta\beta\)) state no nuclear spin flip can occur for the all-\(\beta\) nuclear spin state. For a positive hyperfine interaction, this means that the highest field line has a zero contribution from this mechanism. There is another, hyperfine-
independent part, that contributes to ST\textsubscript{-1} polarization.\textsuperscript{31} This is due to the fact that one of the radicals in its particular hyperfine state may interact with the other radical in all of its hyperfine states, giving rise to a net emission polarization for a triplet state precursor. Combined, the polarization pattern due to the ST\textsubscript{-1} RPM for a triplet state precursor is totally emissive with a stronger polarization for the lowest field line than for the highest field one.

![Figure 2.4 Diabatic potential energy curves of the singlet (S) and triplet levels of a radical pair, separated by twice the exchange energy (J) as a function of interradical distance. ST\textsubscript{0} and ST\textsubscript{-1} indicate positions at which hyperfine interaction induced mixing may occur between mentioned levels.](image)

**Figure 2.4** Diabatic potential energy curves of the singlet (S) and triplet levels of a radical pair, separated by twice the exchange energy (J) as a function of interradical distance. ST\textsubscript{0} and ST\textsubscript{-1} indicate positions at which hyperfine interaction induced mixing may occur between mentioned levels.

**Hyperfine independent CIDEP mechanisms**

*Triplet Mechanism (TM)*\textsuperscript{32}

As was mentioned in chapter 1, intersystem crossing (ISC) rates depend on the symmetries of the states involved, as well as on that of the spin–orbit coupling Hamiltonian. In the absence of a magnetic field the three triplet states (T\textsubscript{x}, T\textsubscript{y} and T\textsubscript{z}) are not degenerate due to dipolar coupling of the two electrons. This means that in the absence of a magnetic field ISC can be anisotropic, *i.e.* one of the triplet sublevels is populated preferably (Figure 2.5). In a magnetic field the triplet sublevels are governed by the direction of this field. Since the molecule rotates in solution, no preferential population of any of the triplet sublevels (T\textsubscript{0}, T\textsubscript{±1}), separated by the Zeeman splitting, is expected. However, since for *organic* molecules in the magnetic field of an X-band spectrometer, the zero-field and Zeeman splittings are of the same order of magnitude, some correlation between the two descriptions of the triplet states does exist. This correlation becomes stronger when the rotational correlation time is increased, *i.e.* in more
viscous solvents. The excess population of one of the triplet sublevels translates into excess population in one of the spin levels of the free radical (Figure 2.5), creating a net emission or absorption effect in the EPR spectrum. However if the radical formation is slower than the spin–lattice relaxation decay (typically a few nanoseconds) of the triplet spin polarization, no TM spin polarization is observed. Then, the spin distribution in the free radicals depends on the Boltzmann equilibrium spin distribution in the triplet excited state. On the other hand, if the triplet excited state is too short-lived, i.e. shorter than the order of one precession turn (100 ps at 10 GHz), the energies of the triplet sublevels become uncertain and again no spin polarization in the free radicals is generated. This creates a time window that the photochemical reaction rate has to be in, in order for the TM to operate.

![Figure 2.5 Schematic overview of the important processes in the Triplet Mechanism (TM) induced spin polarization.](image)

**Spin–Orbit Coupling Mechanism (SOCM)**

The radical pair in its triplet state can only convert to its singlet state by intersystem crossing when in close contact. Since ISC-rates are spin-sublevel selective, this leads to selective depopulation of some of the triplet sublevels in the contact radical pair. If the remaining triplet contact radical pairs subsequently proceed to disintegrate into free radicals, hyperfine independent spin polarization will have been generated. This mechanism can be distinguished from the TM, since in SOCM the presence of heavy atoms will increase the polarization, but decrease the radical formation yield.
2.3 (Spectro)electrochemistry

Since in photochemical and redox reactions the same (frontier) orbitals may be involved, data from reversible electrochemical processes can supplement those from photochemical measurements. For instance, the difference between reduction and oxidation potentials is often used as an indication for the energy difference between the zeroth vibrational levels of ground and excited states. Furthermore, some photoproducts (e.g. radicals) can be conveniently generated by electrochemical methods and transient species (e.g. D*–A− states) observed in time-resolved spectra can be assigned by recording the spectra of electrochemical oxidation and reduction of the donor and acceptor moieties, respectively. Finally, in situ electrogenerated species may have interesting photophysical and photochemical properties themselves.

The commonly used method for the determination of oxidation and reduction potentials is cyclic voltammetry (CV). In this experiment the voltage applied to a sample solution with added electrolyte is scanned, while recording the current. At a certain predefined potential the scan direction is reversed (hence: cyclic voltammetry). Initially, assuming no electrode process occurs and the solution resistance is close to zero, no current flows. Once the potential reaches a value at which the sample compound is oxidized or reduced, the current rises. Since the solution is not stirred, the concentration of the parent compound in the thin layer near the working electrode surface (the electrode double layer) decreases. At a certain potential the concentration gradient is steepest and the diffusion-controlled Nernstian current reaches a maximum. The parent compound has then been exhaustively electrolyzed at the electrode surface. Continued sweeping of the potential shifts the zone of electrolysis further to the bulk solution, the concentration gradient drops again and the Faradaic current decreases exponentially to the mass transport limiting value. Figure 2.6 displays a typical example of a cyclic voltammogram. Apart from a working electrode and a counter electrode, some means must be devised to determine the applied potential. For the CV measurements presented in this thesis, a silver wire was employed as a pseudo-reference electrode. Since the potential of such an electrode varies with temperature and chemical composition of the solution, all potentials are given relative to the redox potential of the Fc/Fc+ couple (Fc = ferrocene) used as an internal standard. Many types of absolute reference electrodes exist, e.g. saturated calomel electrodes (SCE). However, these suffer

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from the disadvantage that they cannot be used in air-tight, evacuable CV-cells of the type used in this thesis.

![Cyclic Voltammogram](image)

**Figure 2.6** Typical example of a cyclic voltammogram.

CV does not provide any specific information on bonding and electronic properties. However, since oxidized and reduced species have their own spectroscopic (UV/Vis, IR, EPR, resonance Raman, etc.) properties, the combination of cyclic voltammetry and spectroscopic techniques is a powerful one. Spectroelectrochemistry (IR, UV/Vis) has advanced hugely since the development of optically transparent thin layer electrochemical (OTTLE) cells. The working electrode of such a cell usually consists of a transparent wire mesh, rather than a solid surface.\(^{42,43}\) Spectroelectrochemical techniques at various temperatures are used in chapter 4.

### 2.4 Quantum chemical calculations\(^ {44,45}\)

#### 2.4.1 Introduction

The investigations described in this thesis make use of quantum chemical calculations in several instances, in order to clarify the electronic structure of the complexes under study, to assign low-lying electronic transitions and to assign bands observed in resonance Raman spectra. This section attempts to give a very brief introduction in quantum chemical calculations in general and density functional methods in particular.
In quantum chemical calculations one generally aims to solve the famous Schrödinger equation (eq. 2.7):

\[ \hat{H} \psi = E \psi \]

in which

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_i \sum_{j \neq i} \frac{1}{|r_i - r_j|} \]  

Although elegant in its simplicity, it is analytically unsolvable for multi-electron systems. The first two terms of the Hamiltonian, describing the kinetic energy of the entire system and the potential energy due to the electrostatic interaction of the electrons with the nuclei do not pose any problems, in contrast to the third term, which describes the electron–electron interaction. Hence, the aim is to approximate this electron–electron interaction in such a way that the equation can be solved, while at the same time giving reliable results. In *ab initio* methods, once an approximate model for the molecular electronic wavefunction has been obtained, one proceeds to perform the calculations rigorously without further approximations. As this gives rise to lengthy calculations especially for large molecules, simplified methods have been developed in which experimental information is used in the calculation to obtain accurate information about electronic structures and so on. These latter methods are collectively known as semi-empirical methods.

A common first approximation of the electron–electron interaction is that each electron moves in an average field of the other electrons. In this way the n-electron equation can be separated into n one-electron equations. A frequently used way to solve these equations is by the self-consistent field (SCF) method, starting with a set of guess orbitals from which the operator can be constructed. Solution of the n one-electron equations yields a new set of orbitals, which can in turn be used to adjust the operator. This iterative process continues until the obtained orbitals remain constant.

However, by approximating the electron–electron interaction as described above, it was assumed that each electron moves independently, thus neglecting electron correlation. Several ways have been developed to make post-SCF corrections that approximate electron correlation in some way, such as configuration interaction (CI) and Møller-Plesset
perturbation methods, e.g. MP2. The calculations described in this thesis were performed by a different approach, known as density functional theory.

2.4.2 Density Functional Theory\textsuperscript{46,47}

Density functional theory (DFT) deals with electron densities rather than wavefunctions. This theory is based on the theorem that the total energy of a system is a functional of the system's electron density.\textsuperscript{48} In general a functional is the integration of a function over space. If this function contains first or higher derivatives, integration yields a non-local functional.

Rather than solving the Schrödinger equation, in DFT-calculations the aim is to minimize the energy functional, which reduces calculational costs \textit{enormously}, compared to conventional \textit{ab initio} methods. This energy functional can be written as a sum of functionals describing the kinetic energy, the electrostatic interaction between electrons and nuclei, the repulsion of each electron moving in the average field of all the other electrons and, finally, the electron exchange and correlation interaction.\textsuperscript{49} A self-consistent field approach (see above) can be taken to perform the calculation. The last term, the electron exchange and correlation energy functional has to be approximated and it is the quality of this approximation that determines the quality of the results of the calculation. A popular method is the local density approximation, in which one assumes that the system can be approximated locally by a homogeneous electron gas. Additionally, more accurate functionals have been developed, on which most of the success of the DFT-method is based. Another important factor is the choice of basis sets; molecular orbitals can be represented by a linear combination of one-electron orbitals or basis functions, which is called the basis set. A great deal of effort is being put into the development of better basis sets. Over the last 20 years, time-dependent DFT-methods were developed,\textsuperscript{50} which have been implemented recently in some program packages. These methods, which give access to properties such as Raman intensities and excitation energies are also used in chapter 7 of this thesis.
2.5 References

Chapter 2. Research Methods and Backgrounds


Tuning the Excited State Properties of $[M(SnR_3)_2(CO)_2(\alpha$-diimine)] ($M = Ru, Os; R = Me, Ph$)

3.1 Abstract

The influences of R, the α-diiimine and the transition metal M on the excited state properties of the complexes \([M(SnR_3)_2(CO)_2(\alpha\text{-diiimine})]\) (M = Ru, Os; R = Ph, Me) were investigated. Various synthetic routes were used to prepare the complexes, which all possess an intense Sigma-Bond-to-Ligand Charge Transfer band in the visible region corresponding to a transition from a \(\sigma(Sn-M-Sn)\) to a \(\pi^*(\alpha\text{-diiimine})\) orbital. The resonance Raman spectra show that many bonds are only weakly affected by this transition. The room temperature time-resolved absorption (TA) spectra of \([M(SnR_3)_2(CO)_2(dmb)]\) (M = Ru, Os; R = Me, Ph; dmb = 4,4'-dimethyl-2,2'-bipyridine) show the absorptions of the radical anion of dmb, in line with the SBLCT-character of the lowest excited state. The excited state lifetimes at room temperature vary between 0.5 and 3.6 μs and are mainly determined by the photolability of the complexes. All complexes are photostable in a glass at 90 K, under which conditions they emit with very long lifetimes. The extremely long emission lifetimes (e.g. \(\tau = 1.1\) ms for \([Ru(SnPh_3)_2(CO)_2(dmb)]\)) are about a thousand times longer than those of the \(^3\text{MLCT}\) states of the \([Ru(Cl)(Me)(CO)_2(\alpha\text{-diiimine})]\) complexes. This is due to the weak distortion of the former complexes in their \(^3\text{SBLCT}\) states as seen from the very small Stokes shifts. Remarkably, replacement of Ru by Os hardly influences the absorption and emission energies of these complexes; yet the emission lifetime is shortened due to an increase of spin–orbit coupling (SOC). The quantum yield of emission at 90 K is 1 – 5% for these complexes, which is lower than might be expected on the basis of their slow non-radiative decay.

3.2 Introduction

Most coordination and organometallic compounds containing a low-valent transition metal and an α-diiimine ligand such as 2,2'-bipyridine (bpy) possess intense low-energy Metal-to-Ligand Charge Transfer (MLCT) transitions in the visible region of the spectrum. Best known are \([Ru(bpy)_3]^{2+}\) and \([Re(Cl)(CO)_3(bpy)]^{3+}\) which proved to be good photosensitzers for energy and electron transfer processes. Although \([Ru(bpy)_3]^{2+}\) is more suitable as a photosensitizer due to its longer excited state lifetime and greater stability of its oxidation product, the \([Re(L)(CO)_3(\alpha\text{-diiimine})]^{+0}\) complexes are more flexible since the
ligand L can be varied at will,\(^4\) giving rise to large variation in excited state properties. Thus, when \(L = \text{Cl}^-\) is replaced by \(L = \Gamma\), the HOMO obtains predominant halide character and the low-energy transitions change character from MLCT or \(d_{\pi}(\text{Re}) \rightarrow \pi^*(\alpha\text{-diimine})\) to Halide-to-Ligand Charge-Transfer (XLCT) or \(\pi^*(\alpha\text{-diimine}) \rightarrow \pi^*(\alpha\text{-diimine})\).\(^5\) Yet another situation arises if L is an alkyl or metal fragment bound to Re via a high-lying \(\sigma(\text{Re-L})\) orbital. The lowest excited state then has \(\sigma(\text{Re-L})\pi^*(\alpha\text{-diimine})\) or Sigma-Bond-to-Ligand Charge Transfer (SBLCT) character.\(^6\) The SBLCT states are normally shorter lived than the MLCT and XLCT states since they give rise to homolysis of the metal–metal or metal–alkyl bond with formation of radicals. For quite a few \([\text{Re(L)(CO)}_3(\alpha\text{-diimine})]\)+ complexes these radicals and their formation have been studied with (time-resolved) spectroscopic techniques.\(^6,7\)

Interestingly, most of these complexes are not only photostable at low temperature, but their \(^3\)SBLCT states are also much longer lived than \(^3\)MLCT or \(^3\)XLCT states usually are. For instance, \([\text{Re(Br)(CO)}_3(\text{dmb})]\) (dmb = 4,4′-dimethyl-2,2′-bipyridine) emits in a 2-MeTHF glass at 80 K from its mixed \(^3\)MLCT/\(^3\)XLCT state at 525 nm with a lifetime of 3.7 \(\mu\)s, whereas \([\text{Re(SnPh}_3)(\text{CO})_3(\text{dmb})]\) emits from its \(^3\)SBLCT state at 609 nm with a lifetime of \(1.1 \times 10^2\) \(\mu\)s under these conditions.\(^5,6\)

In order to further increase the variation in excited state properties we have extended our photochemical studies to complexes of the type \([\text{Ru(L}_1)(L_2)(\text{CO})_2(\alpha\text{-diimine})]\), in which both \(L_1\) and \(L_2\) can be varied.\(^8\) Especially those complexes proved to be of great interest in which both \(L_1\) and \(L_2\) are bound to Ru by a high-lying \(\sigma\) orbital. The HOMO of these complexes is a \(\sigma(L_1\text{-Ru-L}_2)\) orbital and, accordingly, the lowest-energy transition has \(\sigma(L_1\text{-Ru-L}_2) \rightarrow \pi^*(\alpha\text{-diimine})\) (SBLCT) character. Depending on the relative strengths of the Ru–L\(_1\) and Ru–L\(_2\) bonds and their involvement in the HOMO, one of these bonds is preferably broken on irradiation. If both Ru–L\(_1/L_2\) bonds are strong, as in the case of \(L_1 = L_2 = \text{SnPh}_3\), the complexes proved to be less photoreactive at room temperature and photostable and very long lived in their \(^3\)SBLCT states in a glass at 80 K. In the case of \([\text{Ru(SnPh}_3)(\text{CO})_2(i\text{Pr-DAB})]\) (iPr-DAB = \(N,N^\prime\)-diisopropyl-1,4-diazabutadiene) an emission lifetime of \(2.6 \times 10^2\) \(\mu\)s was measured under these conditions, which is exceptional for charge transfer states of organometallic complexes.\(^8\) This result prompted us to extend our investigations on these complexes further and develop organometallic systems that are photostable at room temperature and emit in the near infrared region with still an appreciable lifetime, to be of use as luminescent labels in biochemical separations. For this purpose, \(\alpha\)-diimine ligands with low-lying \(\pi^*\) orbitals were employed in order to shift the emission to the NIR and to increase

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the barrier for the radical formation. In order to increase the photostability further, Ru was replaced by Os in \([\text{Ru(SnPh}_3)_2(\text{CO})_2(\alpha\text{-diimine})]\) because transition metal atoms from the third row are expected to form stronger bonds with tin than those of the first and second row. Figure 3.1 shows the general structure of the \(\alpha\) -diimine ligands and of the complexes under study.

![Figure 3.1 Schematic structures of the \([\text{M(SnR}_3)_2(\text{CO})_2(\alpha\text{-diimine})]\) complexes and the \(\alpha\)-diimine ligands used.](image)

### 3.3 Experimental Section

**Materials.** \([\text{Ru}_3(\text{CO})_{12}]\) (ABCR), \(\text{K}_2\text{OsCl}_6\) (Alfa), \(\text{I}_2\) (Merck), \(\text{SnClPh}_3\) (Merck, zur Synthese), \(\text{SnClMe}_3\) (Acros, 99%), 4,4'-dimethyl-2,2'-bipyridine (dmb, Fluka), formic acid (Merck) and formaldehyde (aq, 40%, EGA Chemie) were used as received. Solvents purchased from Acros (THF, hexane, dichloromethane, acetonitrile, diethyl ether, methanol, 2-MeTHF), Merck (heptane), BDH (ethanol abs.), Baker (n-propanol) were dried on and distilled from the appropriate drying agent if necessary. Silica gel (kieselgel 60, Merck, 70-230 mesh) for column chromatography was dried and activated by heating in vacuo at 160 °C overnight.

**Syntheses.** All syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. \(N,N'\)-diisopropyl-1,4-diazabutadiene (iPr-DAB),\(^9\) \(N,N'\)-di-(p-methoxyphenyl)-1,4-
Chapter 3. Tuning the Excited State Properties of \([M(SnR_3)_2(CO)_2(\alpha\text{-diimine})](M = Ru, Os)\)
diazabutadiene (pAn-DAB),\(^{10}\) N,N'-bis-(p-methoxyphenylimino)-acenaphthene (pAn-BIAN)\(^{11,12}\) and
[Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)]\(^{13}\) were prepared according to literature procedures.

The complexes [Ru(I)$_2$(CO)$_2$(\alpha\text{-diimine})] (\alpha\text{-diimine} = pAn-DAB, pAn-BIAN, dmb) were
prepared according to the procedure used for the synthesis of [Ru(I)$_2$(CO)$_2$(dmb)]: A mixture of 1.055 g (2.14 mmol) [Ru(I)$_2$(CO)$_2$(MeCN)$_2$] and 442 mg (2.37 mmol) dmb was suspended in 50 mL
diethyl ether and refluxed for 30 minutes. The reaction mixture was cooled down to room temperature
and the residue was filtered off (G3 glass filter), washed with pentane and dried in vacuo to yield
the product as a yellow powder. Yield: 94%. IR (THF); ν(CO) : 2049, 1991 cm$^{-1}$. \(^1^H\) NMR (CDCl$_3$); δ:
2.61 (s, 6H, dmb CH$_3$), 7.38 (d, \(^3^J = 5.5\) Hz, 2H, dmb H5), 8.22 (s, 2H, dmb H3), 8.95 (d, \(^3^J=5.8\) Hz, 2H, dmb H6) ppm. [Ru(I)$_2$(CO)$_2$(pAn-DAB)]: Yield: ca. 90%. IR (THF); ν(CO): 2056, 2002 cm$^{-1}$. \(^1^H\) NMR (CDCl$_3$); δ:
3.88 (s, 6H, OCH$_3$), 6.99 (d, \(^3^J = 9\) Hz, 4H, o-C$_6$H$_4$OCH$_3$), 7.68 (d, \(^3^J = 9\) Hz, 4H, m-C$_6$H$_4$OCH$_3$), 8.12 (s, 2H, imine H) ppm. [Ru(I)$_2$(CO)$_2$(pAn-BIAN)]: Yield: ca. 90%. IR (THF); ν(CO): 2056, 2003 cm$^{-1}$. \(^1^H\) NMR (CDCl$_3$); δ: 3.95 (s, 6H, OCH$_3$), 7.12 (d, \(^3^J = 9\) Hz, 6H, H3+H9, see Figure 3.1 for numbering), 7.52 (pdt, 2H, H4), 7.80 (d, \(^3^J = 8.8\) Hz, 4H, H10), 8.04 (d, 2H, \(^3^J = 8.3\) Hz, H5) ppm.

The polymer [Os(Cl)$_2$(CO)$_2$(dmb)]$_n$ was prepared by a modified literature procedure.\(^{14}\) K$_2$OsCl$_6$
(823 mg, 1.7 mmol) was dissolved in a mixture of formic acid (40 mL) and formaldehyde (aq, 40%, 15 mL). The reaction mixture was deaerated by bubbling nitrogen through for 20 minutes and
subsequently refluxed for 3 days during which the color changed from dark red via greenish to light
yellow. The solvent was removed in vacuo and the resulting product was triturated with dichloromethane. The product was dissolved in acetone and filtered to remove KCl. Evaporation of the
solvent yielded the product as an off-white powder. Yield: ca. 90%. IR (THF); ν(CO): 2117, 2022 cm$^{-1}$.

[Os(Cl)$_2$(CO)$_2$(dmb)]$_n$ was prepared by a modified literature procedure.\(^{14}\) [Os(Cl)$_2$(CO)$_2$(dmb)]$_n$ (269
mg, 0.85 mmol) and dmb (180 mg, 0.97 mmol) were dissolved in 30 mL n-propanol. The reaction
mixture was refluxed for several hours, until IR showed complete conversion. After removing the
solvent in vacuo the product was purified by column chromatography (activated silica, hexane/dichloromethane gradient elution). The product was obtained as a light yellow powder. Yield: ca. 90 %. IR (THF); ν(CO): 2030, 1960 cm$^{-1}$. UV/Vis (THF); \(\lambda_{\text{max}}\): 296, 373 nm. \(^1^H\) NMR (CDCl$_3$); δ: 2.63 (s, 6H, dmb CH$_3$), 7.45 (d, \(^3^J = 5.3\) Hz, 2H, dmb H5), 8.02 (s, 2H, dmb H3), 8.94 (d, \(^3^J = 5.7\) Hz, 2H, dmb H6) ppm.

[Os(Cl)$_2$(CO)$_2$(iPr-DAB)]. [Os(Cl)$_2$(CO)$_2$(iPr-DAB)]$_n$ (201 mg, 0.63 mmol) and iPr-DAB (182.1 mg, 1.30 mmol) were dissolved in 30 mL absolute ethanol. The reaction mixture was refluxed for several hours until IR showed complete conversion. The solvent was evaporated and after purification by column chromatography (activated silica, hexane:THF = 1:1), the product was obtained as an orange powder. Yield: 63 %. IR (THF); ν(CO): 2034, 1965 cm$^{-1}$. UV/Vis (THF); \(\lambda_{\text{max}}\): 419 nm. \(^1^H\) NMR
Chapter 3. Tuning the Excited State Properties of [M(SnR)]2(CO)2(α-diimine)] (M = Ru, Os)

(CDC13; δ: 1.50, 1.52 (d, J = 6.6 Hz, 12H, CH(CH3)2), 4.32 (sept, J = 6.5 Hz, 2H, CH(CH3)2), 8.55 (s, 2H, imine CH) ppm.

[Ru(SnPh)3(CO)2(dmb)]. [Ru(I)2(CO)2(dmb)] (206.2 mg, 0.35 mmol) was dissolved into 25 mL THF. A solution of LiSnPh3 in THF (prepared from SnCIPh3 and freshly cut lithium metal) was added gradually (in the dark) until IR showed complete conversion. Methanol (2 mL) was added to quench any unreacted LiSnPh3. The solvent was evaporated and after purification by column chromatography in the dark (activated silica, hexane/dichloromethane gradient elution), the product was obtained as a red microcrystalline powder. Yield: ca. 50%. Elem. Anal.: calcd. for C50H22Ni2O2RuSn: C 57.67, H 4.07, N 2.69; found C 57.33, H 3.91, N 2.58. FAB-MS; m/z: 1042 [M+] . 965 [M+ - Ph], 691 [M+ - SnPh3]. IR (THF): ν(CO) = 1996, 1942 cm⁻¹. UV/Vis (THF): λmax: 327, 521 nm. ¹H NMR (C₆D₆): δ: 1.65 (s, JSn-H = 9 Hz, 6H, dmb CH₃), 5.80 (d, J = 5.6 Hz, 2H, dmb H5), 6.66 (s, dmb H3), 7.02 (m, 9H, m/p-SnC₆H₅), 7.41 (m, 6H, o-SnC₆H₅), 8.29 (d, J = 5.9 Hz, 2H, dmb H6-6) ppm. ¹³C NMR APT (C₆D₆): δ: 20.2 (dmb Me), 122.8 (dmb C5), 125.4 (dmb C3), 127.1 (p-SnC₆H₅), 127.7 (m-SnC₆H₅), 137.4 (JSn-C = 36Hz, o-SnC₆H₅), 145.1 (dmb C4), 145.4 (dmb C2), 150.7 (JSn-C = 12Hz, ipso-SnC₆H₅), 151.8 (JSn-C = 12Hz, dmb C6), 208.0 (CO) ppm.

[Ru(SnPh)3(CO)2(pAn-DAB)]. To a solution of 285 mg [Ru(I)2(CO)2(pAn-DAB)] in THF, 0.5 mL NaK₅ alloy was added. Stirring at room temperature yielded a solution of a highly reactive anionic intermediate. The remaining NaK₅ alloy was filtered off using a G3 frit and two equivalents of SnCIPh₃ were added in the dark. After column chromatography (activated silica, dichloromethane/hexane gradient elution) the product was obtained as a brownish green powder. Yield: ca. 50%. FAB-MS; m/z: 1126 [M+], 1049 (M+ - Ph), 776 (M+ - SnPh3). IR (THF): ν(CO): 2011, 1960 cm⁻¹. UV/Vis (THF): λmax: 396, 449, 570 nm. ¹H NMR (CDCl₃): δ: 3.18 (s, 6H, OCH₃), 6.33 (d, J = 9 Hz, 4H, o-C₆H₄OCH₃), 6.82 (s, JSn-H = 27 Hz, 2H, imine H), 7.09 (d, J = 9 Hz, 4H, m-C₆H₄OCH₃), 7.19 (m, 18H, m/p-SnC₆H₅), 7.50 (m, 12H, o-SnC₆H₅) ppm. ¹³C NMR APT (CDCl₃): δ: 55.1 (OCH₃), 114.4 (o-C₆H₄OCH₃), 124.5 (m-C₆H₄OCH₃), 127.1 (p-C₆H₄OCH₃), 128 (m/p-SnC₆H₅), 138.0 (JSn-C = 35 Hz, o-SnC₆H₅), 141.3 (ipso-SnC₆H₅), 160.5 (s, JSn-C = 15 Hz, imine C), 204.0 (CO) ppm.

[Ru(SnPh)3(CO)2(pAn-BIAN)]. This complex was prepared from [Ru(I)2(CO)2(pAn-BIAN)] and SnCIPh₃ according to the procedure for [Ru(SnPh)3(CO)2(pAn-DAB)]. Yield: ca. 50%. FAB-MS; m/z: 1250 [M+], 1173 [M+ - Ph], 899 [M+ - SnPh3]. IR (THF); ν(CO): 2011, 1960 cm⁻¹. UV/Vis (THF): λmax: 272, 321, 377sh, 400sh, 455, 607 nm. ¹H NMR (CD₂Cl₂): δ: 3.86 (s, 6H, OCH₃), 6.63 (d, J = 8.7 Hz, 4H, H10, see Figure 1 for numbering), 6.73 (d, J = 7.2 Hz, 2H, H3), 6.9 (m, 18H, m/p-SnC₆H₅), 7.03 (d, J = 8.7 Hz, 4H, H9), 7.24 (m, 12H, o-SnC₆H₅), 7.28 (p, 2H, H4), 7.82 (d, 2H J = 8.4 Hz, H5) ppm. ¹³C NMR APT (CD₂Cl₂): δ: 56.2 (OCH₃), 114.1 (C9, see Figure 3.1 for numbering), 122.8 (C3) 124.6 (C10), 127.7 (C4), 128.1 (p-SnC₆H₅), 128.4 (m-SnC₆H₅), 128.5 (C2), 54
Chapter 3. Tuning the Excited State Properties of \([M(SnR_3)_2(CO)_2(\alpha\text{-diimine})](M = Ru, Os)\)

128.7 (C5), 131.1 (C6), 138.0 \((J_{Sn-C} = 34 \text{ Hz}, o-SnC_6H_5)\), 140.7 (C7), 142.9 \((ipso-SnC_6H_5)\), 144.3 (C8), 159.9 (C11), 161.6 (C1), 204.1 (CO) ppm.

The complexes \([Ru(SnMe_3)_2(CO)_2(\alpha\text{-diimine})](\alpha\text{-diimine} = \text{dmb}, \text{iPr-DAB})\) were prepared by reaction of \([Ru(I)_2(CO)_2(\alpha\text{-diimine})] \) and \(\text{LiSnMe}_3\) according to the procedure used for the synthesis of \([Ru(SnPh_3)_2(CO)_2(dmb)] \) \((\text{vide supra})\). \([Ru(SnMe_3)_2(CO)_2(iPr-DAB)]\). Yield: ca. 50%. IR (THF); \(\nu(CO)\): 1993, 1936 cm\(^{-1}\). UV/Vis (THF); \(\lambda_{max}\): 277, 404, 511 nm. \(^1\)H NMR (CDCl\(_3\)); \(\delta\): 0.03 (s, \(J_{Sn-H} = 43 \text{ Hz}\), 18H, SnMe), 1.38 (d, \(J = 6.6 \text{ Hz}\), CH(CH\(_3\))\(_2\)), 4.47 (sept, 2H, \(J = 6.6 \text{ Hz}\), CH(CH\(_3\))\(_2\)), 7.82 (s, \(J_{Sn-H} = 26 \text{ Hz}\), 2H, imine H) ppm. \(^{13}\)C NMR APT (C\(_6\)D\(_6\)); \(\delta\): -8.5 \((J_{Sn-C} = 198 \text{ Hz}, \text{SnC}_6H_5)\), 25.0 \((CH(CH_3)_2)\), 141.6 (imine-C), 181.5 \((J_{Sn-C} = 48 \text{ Hz}, \text{CO})\) ppm.

\([Ru(SnMe_3)_2(CO)_2(dmb)]\). Yield: ca. 50%. IR (THF); \(\nu(CO)\): 1984, 1928 cm\(^{-1}\). UV/Vis (THF); \(\lambda_{max}\): 257sh, 409, 598 nm. \(^1\)H NMR (CDCl\(_3\)); \(\delta\): 0.10 (s, \(J_{Sn-H} = 38 \text{ Hz}\), 18H, SnMe 2.63 (s, \(J_{Sn-H} = 11 \text{ Hz}\), 6H, dmb CH\(_3\)), 6.07 (d, \(J = 5.9 \text{ Hz}\), 2H, dmb H-5), 7.08 (s, 2H, dmb H3), 8.70 (d, \(J = 5.9 \text{ Hz}\), 2H, dmb H6) ppm. \(^{13}\)C NMR APT (C\(_6\)D\(_6\)); \(\delta\): -10.1 \((\text{SnMe})\), 20.5 \((\text{dmb CH}_3)\), 122.8 \((J_{Sn-C} = 13 \text{ Hz}, \text{dmb C5})\), 124.4 \((J_{Sn-C} = 8 \text{ Hz}, \text{dmb C3})\), 144.3 \((J_{Sn-C} = 16 \text{ Hz}, \text{dmb C4})\), 149.7 \((J_{Sn-C} = 16 \text{ Hz}, \text{dmb C2})\), 151.5 \((J_{Sn-C} = 12 \text{ Hz}, \text{dmb C6})\). \([Ru(SnMe_3)_2(CO)_2(dmb)]\).

\([Os(SnPh_3)_2(CO)_2(dmb)]\). \([Os(\text{Cl})_2(CO)_2(dmb)]\) (332.4 mg, 0.66 mmol) was dissolved into 25 mL THF. A solution of \(\text{LiSnPh}_3\) in THF (prepared from SnClPh\(_3\) and freshly cut lithium metal) was added gradually (in the dark) until IR showed complete conversion. Methanol (2 mL) was added to quench any unreacted \(\text{LiSnPh}_3\). The solvent was evaporated and after purification by column chromatography in the dark (silica, hexane/dichloromethane gradient elution) the product was obtained as a red microcrystalline powder. Yield: ca. 50%. FAB-MS; \(m/z\): 1130 \([M^+\text{-Ph}]\), 781 \([M^+\text{-SnPh}_3]\). IR (THF); \(\nu(CO)\): 1989, 1930 cm\(^{-1}\). UV/Vis (THF); \(\lambda_{max}\): 305, 358sh, 514 nm. \(^1\)H NMR (CDCl\(_3\)); \(\delta\): 1.67 (s, \(J_{Sn-H} = 9 \text{ Hz}\), 6H, dmb CH\(_3\)), 5.71 (d, \(J = 5.9 \text{ Hz}\), 2H, dmb H5), 6.62 (s, dmb H3), 7.02 (m, 9H, \(m/p-SnC_6H_5\)), 7.41 (m, 6H, \(o-SnC_6H_5\)), 8.45 (d, \(J = 6.0 \text{ Hz}\), 2H, dmb H6) ppm. \(^{13}\)C NMR APT (C\(_6\)D\(_6\)); \(\delta\): 20.1 \((\text{dmb CH}_3)\), 123.1 \((\text{dmb C5})\), 126.2 \((\text{dmb C3})\), 127.2 \((m/p-SnC_6H_5)\), 127.7 \((m/p-SnC_6H_5)\), 137.5 \((J_{Sn-C} = 35 \text{ Hz}, o-SnC_6H_5)\), 144.0 \((J_{Sn-C} = 16 \text{ Hz}, \text{dmb C4})\), 145.2 \((J_{Sn-C} = 13 \text{ Hz}, \text{dmb C2})\), 151.7 \((\text{dmb C6})\), 150.7 \((J_{Sn-C} = 11 \text{ Hz}, ipso-SnC_6H_5)\), 190.8 (CO) ppm.

\([Os(SnPh_3)_2(CO)_2(iPr-DAB)]\). \([Os(\text{Cl})_2(CO)_2(iPr-DAB)]\) (183 mg, 0.40 mmol) was dissolved in 30 mL THF. After addition of NaK-alloy (0.5 mL) the color changed from orange via green to brown-yellow. The reaction mixture was filtered and added in the dark to a solution of 293 mg (0.88 mmol) SnClPh\(_3\) in 10 mL THF. This mixture was stirred for a few minutes and the solvent was removed \textit{in vacuo}. After purification by column chromatography in the dark (silica, hexane/dichloromethane gradient elution) the product was obtained as an orange microcrystalline powder. Yield: ca. 50%. FAB-MS; \(m/z\): 1086 \([M^+\text{-Ph}]\), 1009 \([M^+\text{-Ph}]\), 737 \([M^+\text{-SnPh}_3]\). IR (THF); \(\nu(CO)\): 1996, 1939 cm\(^{-1}\). UV/Vis (THF); \(\lambda_{max}\): 287, 494 nm. \(^1\)H NMR (CDCl\(_3\)); \(\delta\): 0.95 (d, \(J = 6.6 \text{ Hz}\), 12H, CH(CH\(_3\))\(_2\)), 4.62 (sept, \(J = 6.6 \text{ Hz}\), 2H, CH(CH\(_3\))\(_2\)), 7.25 (m, 9H, \(m/p-SnC_6H_5\)), 7.32 (m, 6H,
**Chapter 3. Tuning the Excited State Properties of \([M(\text{SnR})_2(\text{CO})_2(\alpha\text{-diimine})](M = \text{Ru, Os})**

\[\text{o-SnC}_6\text{H}_5, 8.15\) ppm. \[^{13}\text{C} \text{NMR APT (C}_6\text{D}_6); \delta: 24.8 \) ppm. \[\text{CH(CH}_3)_2, 128.0\) \(\text{ppm.} \[\text{C}(\text{CH}_3)]_2, 128.2\) \(\text{ppm.} \]

\[\text{C}_6\text{H}_5\] \(J_{\text{Sn-C}} = 34\) Hz, \(\text{o-SnC}_6\text{H}_5, 142.7\) \(\text{ppm.} \) \[\text{IPS}_{\text{SnC}_6\text{H}_5}, 148.5\) \(\text{ppm.} \]

\[^{13}\text{C} \text{NMR APT (C}_6\text{D}_6); \delta: -9.1\] \(\text{ppm.} \]

\[\text{C}(\text{CH}_3)]_2, 25.2\) \(\text{ppm.} \]

\[\text{CO \text{ppm.} \]}

\[^{31}\text{P} \text{NMR APT (C}_6\text{D}_6); \delta: -9.1\] \(\text{ppm.} \]

\[\text{C}(\text{CH}_3)]_2, 25.2\) \(\text{ppm.} \]

\[^{31}\text{P} \text{NMR APT (C}_6\text{D}_6); \delta: -9.1\] \(\text{ppm.} \]

**Spectroscopic Measurements.** All spectroscopic measurements were performed under a nitrogen atmosphere. Infrared spectra were recorded on Bio-Rad FTS-7 and FTS-60A FTIR spectrophotometers (the latter equipped with a liquid-nitrogen-cooled MCT detector), and electronic absorption spectra on Varian Cary 4E and Hewlett-Packard 8453 spectrophotometers. NMR spectra were recorded on a Bruker AMX 300 (300.13 MHz and 75.46 MHz for \(^1\text{H}\) and \(^{13}\text{C}\), respectively) spectrometer. Resonance Raman spectra of the complexes dispersed in KNO₃ pellets were recorded on a Dilor XY spectrometer equipped with a Wright Instruments CCD detector, using a Spectra Physics 2040E Ar⁺ in combination with Coherent CR490 and CR590 dye lasers (with Coumarin 6 and Rhodamine 6G dyes) as the excitation sources. Steady state emission spectra were measured on a SPEX Fluorolog 2 (equipped with an RCA C31034 Peltier cooled GaAs photomultiplier).

Nanosecond time-resolved electronic absorption and emission spectra were obtained using a setup described previously. A teflon mask around the glass tube sample cell with 1 mm holes for the probe light and a 1 cm slit for the pump light was used for the low-temperature transient absorption spectrum. As irradiation sources the second harmonic (532 nm) of a Spectra Physics GCR3 Nd:YAG laser, a Quanta Ray PDL pulsed dye laser with a Coumarin 440 solution (440 nm) or a continuously tunable (400-700 nm) Coherent Infinity XPO laser were used. Emission quantum yields were measured relative to a standard solution of [Re(Cl)(CO)₃(bpy)] in 2-MeTHF (Φ = 0.028 at 77 K), using a gate of 10 ms.

Time-resolved IR measurements were performed at the University of Nottingham. The detailed description of the step-scan apparatus developed at the University of Nottingham will be published elsewhere. The set-up consists of a commercially available step-scan FTIR spectrometer (Nicolet Magna 860) equipped with a 100 MHz 12-bit digitizer and a 50MHz MCT detector. The sample was excited using the second (532 nm) or third (355 nm) harmonic from a Nd:YAG laser (Spectron SL80SG). The data collection was performed with OMNIC software. Synchronization of the Nd:YAG laser with data collection was achieved by means of a pulse generator (Stanford DG535). The signal passes a low-noise pre-amplifier (Stanford Research System, Model SR560) which has
been set up at 1MHz for our experiments. Experiments at 77K were performed in a home-built IR cell, with CaF2 windows. Typically, a 1mm pathlength was used.

Photochemical quantum yields were determined by observation of the decay of the first absorption band of solutions of the complexes in dichloromethane at 21.0 °C by in situ irradiation in a Varian Cary 4E spectrophotometer using previously described procedures.7

3.4 Results

3.4.1 Syntheses

The procedure used for the synthesis of [Ru(SnPh3)2(CO)2(iPr-DAB)]16 is not suitable for the preparation of the [Ru(SnR3)2(CO)2(α-diimine)] complexes containing other α-diimine ligands than R–DAB. Instead, these complexes were prepared from [Ru(I)2(CO)2(α-diimine)]17, which was obtained by reaction of the appropriate α-diimine ligand with [Ru(I)2(CO)2(MeCN)2], and LiSnR3.

However, during the preparation of [Ru(SnPh3)2(CO)2(pAn–BIAN)] the last step resulted in decomposition. [Ru(I)2(CO)2(pAn–BIAN)] was therefore prepared first and subsequently reduced using sodium-potassium alloy to give a highly reactive intermediate. This intermediate was then allowed to react with two equivalents of SnClPh3, yielding the desired product. This method, which has also been used for the synthesis of [Ru(Me)(I)(CO)2(bpy)]18,19 was also successfully used for the synthesis of [Ru(SnPh3)2(CO)2(pAn–DAB)].

The recently synthesized complexes [Os(Cl)2(CO)2(α-diimine)],14 proved to be excellent starting compounds for the preparation of [Os(SnPh3)2(CO)2(α-diimine)]. The synthesis started with the formation of the polymer [Os(Cl)2(CO)2]n which was allowed to react with the α-diimine ligand. Subsequent addition of LiSnPh3 to a solution of this complex afforded [Os(SnPh3)2(CO)2(α-diimine)] in the case of dmb. However, in the case of the iPr–DAB complex, the last step of this reaction sequence resulted in decomposition and [Os(SnPh3)2(CO)2(iPr–DAB)] was therefore synthesized from [Os(Cl)2(CO)2(iPr–DAB)] using the procedure used for [Ru(SnPh3)2(CO)2(pAn–BIAN)].

All compounds are strongly coloured microcrystalline powders. They have a trans-(SnR3, SnR3), cis-(CO, CO)-configuration, as can be seen from their IR and NMR spectra.13
The complexes are photostable in the solid state, but photolabile in solution to varying degrees.

3.4.2 Electronic absorption and resonance Raman spectra

All complexes under study show an intense absorption band at 500 – 600 nm (Table 3.1), which has been assigned to a σ(Sn–Ru–Sn)→π*(iPr-DAB) Sigma-Bond-to-Ligand Charge Transfer (SBLCT) transition in the case of [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)]. The absorption bands are only weakly solvatochromic. For instance, ∆ν = $ν_{\text{max}}$(MeCN) – $ν_{\text{max}}$(toluene) = 0.57 x 10$^3$ cm$^{-1}$ for [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)], which is much less than the solvatochromism of the MLCT band of e.g. the isostructural complex [Ru(Cl)(Me)(CO)$_2$(iPr-DAB)] (∆ν = 1.9 x 10$^3$ cm$^{-1}$). Furthermore, the absorption bands of the R-DAB and pAn-BIAN complexes (Table 3.1, entries 1, 2, 5, 7 and 9) are less solvatochromic (∆ν = 0.2 x 10$^3$ – 0.6 x 10$^3$ cm$^{-1}$) than those of the aromatic dmb complexes (∆ν = 1.2 x 10$^3$ – 1.5 x 10$^3$ cm$^{-1}$) (Table 3.1, entries 4, 6 and 8).

Table 3.1 Electronic absorption spectral data and transient absorption lifetimes of the M(SnR$_3$)$_2$(CO)$_2$($\alpha$-diimine) complexes at room temperature.

<table>
<thead>
<tr>
<th>entry</th>
<th>metal</th>
<th>R</th>
<th>$\alpha$-diimine</th>
<th>electronic absorption; $\lambda_{\text{max}}$ (nm)</th>
<th>transient lifetime$^c$ (μs)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>toluene</td>
<td>CH$_2$Cl$_2$ (ε)$^a$</td>
<td>MeCN</td>
</tr>
<tr>
<td>1$^d$</td>
<td>Ru</td>
<td>Ph</td>
<td>iPr-DAB</td>
<td>523</td>
<td>519 (6.8)</td>
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<tr>
<td>2</td>
<td>Ru</td>
<td>Ph</td>
<td>pAn-DAB</td>
<td>577</td>
<td>572 (2.7)</td>
</tr>
<tr>
<td>3</td>
<td>Ru</td>
<td>Ph</td>
<td>pAn-BIAN</td>
<td>614</td>
<td>605 (16)</td>
</tr>
<tr>
<td>4</td>
<td>Ru</td>
<td>Ph</td>
<td>dmb</td>
<td>542</td>
<td>529 (3.8)</td>
</tr>
<tr>
<td>5</td>
<td>Ru</td>
<td>Me</td>
<td>iPr-DAB</td>
<td>517</td>
<td>515 (7.2)</td>
</tr>
<tr>
<td>6</td>
<td>Ru</td>
<td>Me</td>
<td>dmb</td>
<td>630</td>
<td>612 (5.3)</td>
</tr>
<tr>
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<td>Os</td>
<td>Ph</td>
<td>iPr-DAB</td>
<td>497</td>
<td>495 (6.2)</td>
</tr>
<tr>
<td>8</td>
<td>Os</td>
<td>Ph</td>
<td>dmb</td>
<td>537</td>
<td>519 (4.1)</td>
</tr>
<tr>
<td>9</td>
<td>Os</td>
<td>Me</td>
<td>iPr-DAB</td>
<td>485</td>
<td>484 (6.9)</td>
</tr>
</tbody>
</table>

$^a$ε in 10$^3$ M$^{-1}$ cm$^{-1}$; $^b$δ = $ν_{\text{max}}$(MeCN) – $ν_{\text{max}}$(toluene) in 10$^3$ cm$^{-1}$; $^c$in THF at room temperature; $^d$from ref 13. $^e$uncertainty large due to overlap of transient and ground state absorptions.

On going to a 2-MeTHF glass at 80K, the absorption bands of the complexes become narrower and shift by ca. 20 nm to shorter wavelengths. They become asymmetric for the R-DAB complexes, while those of the aromatic $\alpha$-diimine compounds show a pronounced
Chapter 3. Tuning the Excited State Properties of \([M(SnR_3)_2(CO)_2(\alpha\text{-diimine})] (M = Ru, Os)\)

shoulder on their short wavelength side. As the DFT-calculations on the model complex \([Ru(SnH_3)_2(CO)_2(H-DAB)]\) do not show the presence of any close-lying electronic transition,\(^6\) this shoulder is attributed to a vibrational sideband.

In order to characterize the SBLCT transition further, we studied the resonance Raman (rR) spectra of the complexes. Upon excitation into an allowed electronic transition, such rR spectra normally show resonance enhancement of Raman intensity for those vibrations which are most strongly coupled to this transition.\(^20\) In other words, this technique allows us to characterize the electronic transition by revealing which bonds of the complex are affected most (see section 2.2.1). RR spectra were recorded for all \([M(SnR_3)_2(CO)_2(iPr-DAB)] (M = Ru, Os; R = Me, Ph)\) complexes under study and for comparison also for \([Ru(Cl)(Me)(CO)_2(iPr-DAB)]\) in order to determine in which way the rR spectra are affected by the type of electronic transition (SBLCT vs. MLCT). The wavenumbers of the most strongly enhanced Raman bands are collected in Table 3.2. The spectrum of \([Ru(Cl)(Me)(CO)_2(iPr-DAB)]\) is rather simple (Figure 3.2A); it shows a strong rR effect for \(v_s(CN)\) of the iPr-DAB ligand at 1573 cm\(^{-1}\) and for a band at 492 cm\(^{-1}\), belonging to a combined \(v(Ru-CH_3)\) and \(v_s(Ru-CO)\) mode (see chapter 8). A weaker effect is observed for \(v_s(CO)\) at 2017 cm\(^{-1}\). This spectrum is characteristic for excitation into an MLCT transition, since such a transition is accompanied by reduction of the iPr-DAB ligand (rR effect for \(v_s(CN)\)) and oxidation of the central metal atom (rR effect for \(v_s(CO)\)).

Table 3.2 Resonance Raman data of the complexes \([M(SnR_3)_2(CO)_2(iPr-DAB)] (M=Ru, Os; R = Ph, Me) and [Ru(Cl)(Me)(CO)_2(iPr-DAB)]\) in KNO\(_3\).

<table>
<thead>
<tr>
<th>metal</th>
<th>R</th>
<th>resonance Raman data</th>
<th>(v_s(CO))</th>
<th>(v_s(CN))</th>
<th>(\delta_s(CH))</th>
<th>(\delta(DAB))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(^2)</td>
<td>Ph</td>
<td>1473s 1283s</td>
<td>1166w 953s 836s 651w 610m</td>
<td>419w 250m 197m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>Ph</td>
<td>1467s 1272s</td>
<td>1168w 958s 844s 657w 614m</td>
<td>424m 256m 211w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>Me</td>
<td>1473s 1286s</td>
<td>1178s 971s 850s 651m 615m 496w 425w 264w 229m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>Me</td>
<td>1470m 1279s</td>
<td>1172s 968s 850s 646w 614m 494w 420m 251w 189w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuClMe(^b)</td>
<td>2017w 1573s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^2\)from ref \(^8\); \(^b\) [Ru(Cl)(Me)(CO)_2(iPr-DAB)], from ref \(^18\)

The bands observed in the rR spectra of the \([M(SnPh_3)_2(CO)_2(iPr-DAB)]\) complexes are weaker than those of \([Ru(Cl)(Me)(CO)_2(iPr-DAB)]\), while more bands are resonantly enhanced. The spectra of e.g. \([Ru(SnPh_3)_2(CO)_2(iPr-DAB))]\) (Figure 3.2B) show rR effects for
stretching and deformation modes of the iPr-DAB ligand (1473, 1283, 953 and 836 cm\(^{-1}\)), while \(\nu_5(\text{CO})\) is not observed at all. Some of these resonance effects are exceptional and their occurrence will be explained in the Discussion Section. In addition, several lower-frequency \(rR\) bands (at 610, 419, 250 and 197 cm\(^{-1}\) for [Ru(SnPh\(_3\))\(_2\)(CO)\(_2\)(iPr-DAB)]) are observed, which belong to (combined) metal–ligand stretching and deformation modes.\(^{21,22}\) The corresponding osmium complex [Os(SnPh\(_3\))\(_2\)(CO)\(_2\)(iPr-DAB)] has virtually the same \(rR\) spectrum, while the spectra of the corresponding [M(SnMe\(_3\))\(_2\)(CO)\(_2\)(iPr-DAB)]) complexes additionally show a strong \(rR\) effect for a band at \(\text{ca. 1170 cm}^{-1}\), which is assigned to a CH\(_3\) deformation mode of the SnMe\(_3\) ligand.\(^{23}\)

Figure 3.2 Resonance Raman spectra of (A) [Ru(Cl)(Me)(CO)\(_2\)(iPr-DAB)] (\(\lambda_{\text{exc}} = 457.9\) nm), (B) [Ru(SnPh\(_3\))\(_2\)(CO)\(_2\)(iPr-DAB)]) (\(\lambda_{\text{exc}} = 457.9\) nm), (C) [Os(SnPh\(_3\))\(_2\)(CO)\(_2\)(iPr-DAB)]) (\(\lambda_{\text{exc}} = 488.0\) nm), (D) [Ru(SnMe\(_3\))\(_2\)(CO)\(_2\)(iPrDAB)]) (\(\lambda_{\text{exc}} = 476.5\) nm) and (E) [Os(SnMe\(_3\))\(_2\)(CO)\(_2\)(iPrDAB)]) (\(\lambda_{\text{exc}} = 476.5\) nm). Asterisks denote NO\(_3^–\) peaks.

3.4.3 Time-resolved electronic absorption and emission spectra

Nanosecond time-resolved absorption (TA) spectra of the complexes were measured in THF at room temperature and for [Os(SnPh\(_3\))\(_2\)(CO)\(_2\)(dmb)] also in a 2-MeTHF glass at 90 K. Both spectra of the latter complex are shown in Figure 3.3. In most spectra the bleaching
of the ground state absorption is not observed due to the much stronger excited state absorption. The TA spectra of all complexes are very similar, and consist of strong absorptions with maxima at ca. 350 and 530 nm, and a weak, broad, band above 600 nm. The low-temperature spectrum of \([\text{Os}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\) shows that this latter absorption is a separate band and not the tail of the 530 nm band. The 90 K spectrum of \([\text{Os}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\) shows that the 530 nm absorption band consists of two components. Similar features, \textit{i.e.} a broad, composite, band around 500 nm, a very broad and weak absorption above 600 nm, and an intense band between 350 and 400 nm, have also been observed in the TA spectra of \([\text{Re}(\text{Br})(\text{CO})_3(\text{dmb})]\), \cite{24} \([\text{Re}(\text{SnPh}_3)(\text{CO})_3(\text{dmb})]\)\cite{25} and \([\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dmb})]\)\cite{26} and in the spectrum of reduced \([\text{Re}(\text{Br})(\text{CO})_3(\text{dmb})]\).\cite{24} They closely resemble the bands found in the absorption spectrum of the \([\text{dmb}]^\ast\) radical anion\cite{27} and are therefore assigned to the intraligand transitions of the \([\text{dmb}]^\ast\) radical anion in the SBLCT states of the complexes. At room temperature the excited states, which have lifetimes varying between 0.5 and 3.6 μs, are quenched by oxygen, which confirms their triplet character. For instance, the transient lifetime of \([\text{Os}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\) is reduced by a factor of ten in the presence of oxygen.

![Figure 3.3](image)

\textbf{Figure 3.3} Transient absorption difference spectra (solid lines) and ground state absorption spectra (dotted lines) of \([\text{Os}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\) in THF at room temperature (A) and in a 2-MeTHF glass at 90 K (B). The delay between the transient absorption difference spectra is 200 ns (A) and 20 μs (B).
Nanosecond time-resolved emission spectra were recorded for the compounds in a 2-MeTHF glass at 90 K, under which conditions the complexes are completely photostable. The emission data (Table 3.3) show that the emitting states of all \( [M(SnR_3)_2(CO)_2(\alpha\text{-diimine})] \) complexes are very long-lived, much longer than the \( ^3\text{MLCT} \) state of the structurally related compound \([\text{Ru}(\text{Cl})(\text{Me})(\text{CO})_2(\text{iPr-DAB})]\). The longest lifetime \((\tau = 1.1 \text{ ms})\) is observed for \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\), in which complex the dmb is a rigid aromatic ligand. The SnMe\(_3\) substituted complexes have slightly shorter emission lifetimes than the SnPh\(_3\) ones, which was previously observed for \([\text{Re}(\text{SnR}_3)(\text{CO})_3(\text{phen})]\) \((R = \text{Me, Ph}).^{26}

Figure 3.4 shows the absorption and excitation spectra of \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\), together with its CW emission spectrum excited at 500 nm. The excitation spectrum does not deviate from the absorption spectrum, which means that the population of the emissive state has the same efficiency throughout the first absorption band.

![Emission spectrum, excitation spectrum, and ground state absorption spectrum](image)

**Figure 3.4** Emission spectrum (solid line, \(\lambda_{\text{exc}} = 500 \text{ nm}\)), excitation spectrum (dashed line, \(\lambda_{\text{em}} = 620 \text{ nm}\)) and ground state absorption spectrum (dotted line) of \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{dmb})]\) in a 2-MeTHF glass at 90 K.

Just as for \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{iPr-DAB})]\)^8 a weak emission is observed at the low-energy side of the broad emission band, which is only produced by excitation at the low-energy side of the first absorption band. Its lifetime is somewhat shorter than that of the much
stronger high-energy component. For instance, the emission of $[\text{Ru(SnPh}_3)_2(\text{CO})_2(\text{dmmb})]$ has a lifetime of 1.1 ms at 440 nm excitation (Table 3.3) and 0.76 ms at 532 nm excitation. As the lifetimes do not differ much, taking into account the difference in emission energy, both emissions most likely belong to the same excited state of the complex in a different environment or isomeric form. The former explanation was e.g. given in the case of $[\text{Re(SnPh}_3)(\text{CO})_3(\text{bpy})]$, since the effect was not observed for this complex in its solid state.\textsuperscript{26} Variable excitation wavelength time-resolved emission measurements, using a continuously tuneable Coherent Infinity XPO laser, showed that both the emission maximum and lifetime are constant for excitation wavelengths covering most of the absorption band and only start to change at the extreme long-wavelength side of the absorption band.

Table 3.3 Emission data of $[\text{M(SnR}_3)_2(\text{CO})_2(\alpha\text{-diimine})]$ and $[\text{Ru(Cl)(Me)(CO)}_2(i\text{Pr-DAB})]$ in a 2-McTHF glass at 90 K.

<table>
<thead>
<tr>
<th>entry</th>
<th>metal</th>
<th>$\text{R}^\alpha$</th>
<th>$\alpha$-diimine</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Delta E_{\text{abs-em}}$ ($10^3 \text{ cm}^{-1}$)</th>
<th>$\tau$ ($10^{-2} \mu\text{s}^{-1}$)</th>
<th>$\Phi_{\text{em}}$</th>
<th>$\phi_{\text{NC}}$</th>
<th>$k_{\text{er}}$ ($10^3 \text{ s}^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>Ph</td>
<td>iPr-DAB</td>
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<td>633</td>
<td>5.3</td>
<td>2.6</td>
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</tr>
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<tr>
<td>7</td>
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<td>Ph</td>
<td>iPr-DAB</td>
<td>478</td>
<td>655</td>
<td>5.7</td>
<td>0.32</td>
<td>0.58</td>
<td>1.8</td>
<td>3.13</td>
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<td>dmb</td>
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<td>589</td>
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<td>iPr-DAB</td>
<td>478</td>
<td>714</td>
<td>6.9</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru(Cl)(Me)(CO)}_2(i\text{Pr-DAB})]^b$</td>
<td>387</td>
<td>650</td>
<td>10</td>
<td>0.003</td>
<td>0.034</td>
<td>11</td>
<td>384</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^\alpha$from ref\textsuperscript{8}, $^b$from ref\textsuperscript{48}

Replacement of ruthenium by osmium has only a small effect on the absorption and emission energies of the $[\text{M(SnR}_3)_2(\text{CO})_2(\alpha\text{-diimine})]$ complexes. In spite of this, the emission lifetimes of the Os complexes are much shorter, due to the increase of spin–orbit coupling (SOC) going from Ru to Os. For all complexes the quantum yields of emission (Table 3.3) from the $^5\text{SBLCT}$ states are rather low in view of their very long emission lifetimes. In the next section we will discuss this observation and its consequences in more detail.
In the time-resolved FTIR spectra (Figure 3.5), the difference between iPr-DAB and dmb complexes is clearly visible. Thus, the excited state IR spectrum of [Os(SnPh_3)_2(CO)_2(iPr-DAB)] is very similar to that of [Ru(SnPh_3)_2(CO)_2(iPr-DAB)], i.e. the $\nu$(CO) bands have shifted to slightly lower wavenumbers. Apparently, in the excited state, the $\alpha$-diimine ligand is a poorer $\pi$-acceptor, which increases $\pi$-backbonding to CO. In contrast, in the excited states of the two dmb complexes [M(SnPh_3)_2(CO)_2(iPr-DAB)] ($M$ = Ru, Os), the $\nu$(CO) bands have shifted to higher wavenumbers. This indicates that $\pi$-backbonding to CO has decreased, although the frequency shift is far less than observed for the MLCT states of e.g. [Re(Cl)(CO)_3(bpy)]. Work is in progress to clarify this difference.

![Figure 3.5 Transient IR difference spectra of (A) [Os(SnPh_3)_2(CO)_2(iPr-DAB)], (B) [Os(SnPh_3)_2(CO)_2(dmb)] and (C) [Ru(SnPh_3)_2(CO)_2(dmb)] in nBuCN/nPrCN (5:4 v/v) at 77 K, $\lambda_{exc}$ = 355 nm. Spectra A and C have been offset by 0.02 and -0.02, respectively, for clarity.](image-url)
3.5 Discussion

The complexes under study belong to a group of α-diimine compounds in which two co-ligands are bound to the central metal atom via high-lying σ orbitals. These co-ligands may be alkyl groups or metal fragments. The lowest-energy transitions of these complexes are fundamentally different from those of complexes with only one such co-ligand, e.g. \([\text{Ru(Cl)(R)(CO)}_2(\alpha\text{-diimine})]\),\(^8\) or \([\text{Ru(Cl)(SnPh}_3](CO)_2(\alpha\text{-diimine})]\).\(^8\) Transitions from the σ(Ru–R) or σ(Ru–Sn) orbitals to \(\pi^*(\alpha\text{-diimine})\) are normally not observed and the lowest-energy transitions of these latter complexes have \(d_\sigma(\text{Ru}) \rightarrow \pi^*(\alpha\text{-diimine})\) (MLCT) character.

This situation changes completely when two metal fragments are coordinated in an axial position to Ru (or Os), as e.g. in the case of \([\text{M(SnR}_3]_2(CO)_2(\alpha\text{-diimine})]\). According to density functional (DFT) MO-calculation on the model complex \([\text{Ru(SnH}_3]_2(CO)_2(H\text{-DAB})]\),\(^16\) the HOMO, denoted as \(σ(\text{Sn–Ru–Sn})\), consists of contributions from the anti-symmetric combination of the Sn fragment σ orbitals Sn(sp\(^3\)-sp\(^3\)) (42%), and from the Ru(5p) (15%) and H-DAB(\(\pi^*\)) (27%) orbitals. This implies a strong σ–\(\pi^*\) interaction, i.e. a large delocalization of electron density from the Sn–Ru–Sn σ-bond over the H-DAB ligand.

According to the calculations, the LUMO of the model complex is also delocalized since it has contributions from H–DAB(\(\pi^*\)) (61%), Ru(4d\(_{yz}\)) (11%) and Sn(sp\(^3\)-sp\(^3\)) (27%). The \(σ(\text{Sn–M–Sn}) \rightarrow \pi^*(\alpha\text{-diimine})\) transition between the HOMO and LUMO is strongly allowed. In view of the nature of the orbitals involved, this transition is called Sigma-Bond-to-Ligand Charge Transfer (SBLCT).\(^27\) Because of the strong σ–\(\pi^*\) interaction, the lowest-energy (SBLCT) transitions of the complexes under study are less solvatochromic than e.g. the MLCT transition of the isostructural complex \([\text{Ru(Cl)(Me)(CO)}_2(i\text{Pr-DAB})]\) (see Table 3.1). The population of \(\pi^*(i\text{Pr-DAB})\) in the ground state, due to the strong σ–\(\pi^*\) interaction, causes a lengthening of the CN-bond and a shortening of the CC-bond, since the lowest \(\pi^*\)-orbital of an α-diimine such as iPr-DAB is anti-bonding between the N and C atoms of the N=C–C=N skeleton and bonding between the central C atoms. This is evident from the crystal structure of \([\text{Ru(SnPh}_3]_2(CO)_2(i\text{Pr-DAB})]\), in which CN- and CC-bond lengths of 1.34 Å and 1.39 Å, respectively, were found. This indicates much more population of \(\pi^*(i\text{Pr-DAB})\) in the ground state than for \([\text{Ru(I)(Me)(CO)}_2(i\text{Pr-DAB})]\) having CN- and CC-bond lengths of 1.26 Å and 1.48 Å, respectively. As can be seen from Table 3.1, the absorption bands of the R–DAB and pAn–BIAN complexes are less solvatochromic than those of the aromatic dmb
Chapter 3. Tuning the Excited State Properties of [M(SnR₃)₂(CO)₂(α-diimine)] (M = Ru, Os)

compounds. This means that the σ and π* orbitals of the dmb complexes have less interaction and, accordingly, their σ(Sn–M–Sn)→π*(α-diimine) (M = Ru, Os) transitions have more charge transfer character. The strong σ–π* interaction of the R–DAB complexes causes the SBLCT transition to occur at higher energy than expected on the basis of its π*-orbital energy. This effect becomes evident when SnPh₃ is replaced by the more electron donating SnMe₃ in the complexes [Ru(SnR₃)₂(CO)₂(α-diimine)] (R = Ph, Me; α-diimine = iPr–DAB, dmb) (Table 3.1). A red shift of the absorption band is then observed in the case of the dmb complexes, but not for the iPr–DAB compounds.

The differences between the [M(SnPh₃)₂(CO)₂(α-diimine)] complexes possessing a low-energy SBLCT transition and the isostructural complex [Ru(Cl)(Me)(CO)₂(iPr–DAB)] having a lowest MLCT transition, are not only reflected in the absorption spectra, but also become evident when their resonance Raman spectra and especially their photophysical and photochemical behavior are compared. The main difference is the observation of rather strong rR effects for a few vibrations in the case of [Ru(Cl)(Me)(CO)₂(iPr–DAB)] and weak rR effects for many vibrations in the case of the [M(SnR₃)₂(CO)₂(iPr–DAB)] complexes. The latter observation confirms the delocalized character of the SBLCT transition during which many bonds are only weakly distorted in the excited state. This weakness of distortion is also demonstrated by the emission spectra (vide infra). The rR spectra of [Ru(SnPh₃)₂(CO)₂(iPr–DAB)] (which is taken as a representative for all the [M(SnR₃)₂(CO)₂(iPr–DAB)] complexes) show strong rR effects for bands at 1473, 1283, 953 and 836 cm⁻¹, while ν₈(CO) is not observed at all. The absence of ν₈(CO) implies that the charge density at the central metal atom is hardly affected by the electronic transition. This result agrees with the main conclusion from the DFT calculations on the model complex [Ru(SnH₃)₂(CO)₂(H–DAB)], that the central metal atom and the carbonyls are hardly involved in the σ→π* (SBLCT) transition.¹⁶ The rR band at 1473 cm⁻¹ is assigned to ν₇(CN), which is lower in frequency than for [Ru(Cl)(Me)(CO)₂(iPr–DAB)] (1568 cm⁻¹), due to the strong π-backbonding to iPr–DAB. The observation of a rR effect for a band at 1283 cm⁻¹ is exceptional. It has only been observed for complexes such as [W(CO)₄(R–DAB)] (R = p-tolyl, mesityl),²⁸ [Re{Re(CO)₅}(CO)₃(iPr–DAB)]²¹ and [Ru(L₁)(L₂)(CO)₂(iPr–DAB)] (L₁, L₂ = metal fragment)⁸,²⁹,³⁰ in which there is a very strong π-backbonding. According to calculations, it is a coupled δₓ(CH) + ν₇(CN) vibration, in which δₓ(CH) is a symmetric in-plane deformation of the imine hydrogen atoms (chapter 8). This coupling, which is responsible for the resonance enhancement of this vibration, can occur because of the small energy difference
between these two local modes. In the case of \([\text{Ru(SnPh}_3)_2(\text{CO})_2(\text{iPr-DAB})]\) strong rR effects are also observed for deformation modes of iPr–DAB at 953 and 836 cm\(^{-1}\). These vibrations are always observed in the case of a strong \(d_{\pi\pi}^\pi\) or \(\sigma^*\pi^*\) interaction (chapter 8). The observation of \(\delta(\text{CH}_3)\) (for the SnMe\(_3\) complexes) indicates that the transition indeed occurs from a \(\sigma(\text{Sn–M–Sn})\) orbital rather than a \(d_{\pi}(\text{M})\) orbital.

According to the TA spectra the complexes \([\text{M(SnPh}_3)_2(\text{CO})_2(\alpha\text{-diimine})]\) have much longer excited state lifetimes at room temperature (\(\tau = 0.5 - 3.6\) \(\mu\)s, Table 3.1) than \([\text{Ru(Cl)(Me)(CO)}_2(\text{iPr-DAB})]\) (\(\tau = 63\) ns\(^{31}\) even though the former complexes are photolabile. This photolability, not observed for \([\text{Ru(Cl)(Me)(CO)}_2(\text{iPr-DAB})]\), is a specific property of complexes having a lowest SBLCT state and involves a homolytic splitting of a M–Sn bond from this state.\(^{32}\) Because of this photolability, the \(^3\)SBLCT states of e.g. \([\text{Ru(SnPh}_3)_2(\text{CO})_2(\text{dmb})]\) and \([\text{Ru(SnPh}_3)_2(\text{CO})_2(\text{iPr-DAB})]\) have accidentally the same lifetimes (Table 3.1) although the dmb ligand is much more rigid and the \(^3\)SBLCT state of its complex is at somewhat higher energy (Table 3.3). The large influence of the photoreactivity on the excited state lifetime becomes also evident when the iPr–DAB ligand is replaced by an \(\alpha\)-diimine with a lower-lying \(\pi^*\) orbital, such as pAn–DAB or pAn–BIAN. The SBLCT states are then lower in energy and, although the energy-gap-law (EGL) predicts a decrease of excited state lifetime, this lifetime becomes much longer due to the larger photostability (Table 3.1). For instance, the quantum yield for the photoreaction of the \([\text{Ru(SnPh}_3)_2(\text{CO})_2(\text{R–DAB})]\) complexes in CH\(_2\)Cl\(_2\) at room temperature is 0.10 for \(\text{R} = \text{iPr}\) but only 0.006 for \(\text{R} = \text{pAn}\). This increase of photostability is most probably due to an increase of the barrier for this reaction, which is already large in the case of \([\text{Ru(SnPh}_3)_2(\text{CO})_2(\text{iPr-DAB})]\).\(^{32}\) As the Os–Sn bonds are stronger than the Ru–Sn bonds, the \([\text{Os(SnPh}_3)_2(\text{CO})_2(\alpha\text{-diimine})]\) complexes are more photostable than the Ru ones (e.g. \(\Phi = 0.038\) for \([\text{Os(SnPh}_3)_2(\text{CO})_2(\text{iPr-DAB})]\) and \(\Phi = 0.10\) for its Ru analogue). As a result, their SBLCT states are also longer lived than those of the Ru compounds, despite the larger spin–orbit coupling constant of the Os atom. Because of their photostability, the lifetimes of the Os complexes at room temperature also increase when iPr–DAB is replaced by dmb, i.e. when the \(\alpha\)-diimine becomes more rigid (Table 3.1).

The differences between the \(^3\)SBLCT states of the \([\text{M(SnPh}_3)_2(\text{CO})_2(\alpha\text{-diimine})]\) complexes and the \(^3\)MLCT state of \([\text{Ru(Cl)(Me)(CO)}_2(\text{iPr-DAB})]\) become even more pronounced at low temperature, under which conditions all complexes are photostable. The emitting \(^3\)SBLCT states of the \([\text{M(SnR}_3)_2(\text{CO})_2(\alpha\text{-diimine})]\) complexes are much longer lived
than the $^3$MLCT state of [Ru(Cl)(Me)(CO)$_2$(iPr-DAB)], an effect which was already noted for the complex [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)]. This increase of lifetime is caused by a decrease of distortion of the complexes in their lowest excited state, which is reflected in a decrease of the apparent Stokes shift (i.e. the energy difference between the absorption and emission maxima, $\Delta E_{abs-em}$; see Table 3.3) from $10 \times 10^3$ cm$^{-1}$ to $(3.5 - 6.0) \times 10^3$ cm$^{-1}$ going from [Ru(Cl)(Me)(CO)$_2$(iPr-DAB)] to [M(SnR$_3$)$_2$(CO)$_2$(a-diimine)]. This implies that for the $^3$SBLCT state the potential energy curve is shifted less with respect to that of the ground state and that the vibrational overlap between these curves is smaller for [M(SnR$_3$)$_2$(CO)$_2$(iPr-DAB)] than for [Ru(Cl)(Me)(CO)$_2$(iPr-DAB)]$^{33-35}$ causing a decrease of the rate constant for non-radiative decay $k_{nr}$. In fact, $k_{nr}$ decreases by a factor of thousand going from [Ru(Cl)(Me)(CO)$_2$(iPr-DAB)] to [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)] (Table 3.3) even though the emission energy hardly changes. Correspondingly, the emission lifetime, which is mainly determined by $k_{nr}$, increases by a factor of ca. one thousand viz. from 0.30 $\mu$s to $2.6 \times 10^2$ $\mu$s.

If an R-DAB ligand is replaced by pAn-BIAN and finally by a fully aromatic ligand the a-diimine becomes more rigid. The complex is then even less distorted in its excited state and this results in a smaller apparent Stokes shift, a smaller value of $k_{nr}$ and a longer emission lifetime. Of course, part of the decrease of $k_{nr}$ is caused by the fact that the dmb complex emits at somewhat higher energy. The rigidity of the dmb ligand, combined with the specific properties of the $^3$SBLCT state, causes the complex [Ru(SnPh$_3$)$_2$(CO)$_2$(dmb)] to have an extremely long emission lifetime of 1.1 ms in a glass at 90 K. Emission lifetimes this long are virtually unknown for charge transfer states of organometallic complexes. Various other types of long-lived excited states are known and they all feature a diminished involvement of the transition metal atom in the excited state. Thus, for Ru(II) a-diimine complexes in which a low-lying intraligand (IL) state interacts with the MLCT state, the excited state lifetime may increase by two orders of magnitude. An example is [Ru(bpy-pyr)(bpy)$_2$]$_2^{2+}$, a [Ru(bpy)$_3$]$_2^{2+}$ type complex in which one bpy ligand has been functionalized with a pyrene group. In this case the MLCT emission decay is biexponential, the longer-lived component ($\tau = 50$ $\mu$s at room temperature) being due to internal conversion from the higher-lying pyrene 1IL state to the $^3$MLCT state.$^{36}$ When an ethynyl group is inserted between the bpy and pyrene units, the IL and MLCT states are in thermal equilibrium, leading to a single exponential decay with a lifetime of 46 $\mu$s.$^{37}$ An even longer excited state lifetime was found for [Ru(CN$_2$-np)(bpy)$_2$]$_2^{2+}$ (CN$_2$-np = naphtho[2,3-f][1,10]phenanthroline-9,14-dicarbonitrile), viz. $\tau = 464$ $\mu$s at 77 K.$^{38}$ Excited states that are virtually purely IL in character can have even longer lifetimes.
Chapter 3. Tuning the Excited State Properties of \([M(SnR_3)_2(CO)_2(\alpha\text{-diimine})] (M = Ru, Os)\)

Examples include various metalloporphyrins and the complexes \([M(bpy)_3]^{3+} (M = \text{Rh, Ir})\). Ligand-to-ligand charge transfer (L'LCT) states, among which the SBLCT states may be reckoned in view of the limited involvement of the transition metal, can be long-lived as well. In the L'LCT state of \([\text{Zn}(4\text{-Cl-PhS})_2(\text{phen})]\) negative charge has been transferred from the thiolate donors to the phenanthroline acceptor. The lifetime of this 3L'LCT state is 8 ms at 6.5 K. For analogous transition metal complexes the excited state lifetime is shorter, e.g. \(\tau = 6.1 \mu\text{s}\) for \([\text{Pt}(bpy)(\text{mnt})]\) (mnt = maleonitriledithiolate) in the solid state at 77 K.

Replacement of ruthenium by osmium has only a small effect on the absorption and emission energies of the \([M(SnPh_3)_2(CO)_2(\alpha\text{-diimine})]\) complexes. Thus, the energy of the 3SBLCT state hardly varies with M. In spite of this, the excited state lifetime is much shorter due to an increase in spin–orbit coupling (SOC). In contrast to this, MLCT states show a decrease of both the emission energy and lifetime when Ru is replaced by Os. For instance, the complex \([\text{Ru}(bpy)_3]\)Cl\(_2\) emits in a 77K ethanol/methanol glass at 584 nm with a lifetime of 5.3 \(\mu\text{s}\), while \([\text{Os}(bpy)_3]\)Cl\(_2\) emits at 710/773 nm with a lifetime of 0.83 \(\mu\text{s}\) under these circumstances. Complexes with a lowest IL state also show a decrease of excited state lifetime going from a second- to a third-row transition metal. For instance, the excited state lifetime of \([M(bpy)_3]^{3+}\) is 2.2 ms for M = Rh, but only 0.080 ms for M = Ir. Likewise, the excited state lifetime of \([M(\text{TPP})]\) (TPP = tetraphenylporphyrine) is 2.8 ms for M = Pd and 0.29 ms for M = Pt.

For all complexes under study the quantum yields of emission \(\Phi_{\text{em}}\) from the 3SBLCT state are rather small in view of their very long emission lifetimes. By using the equation \(\Phi_{\text{em}}/\tau = \Phi_{\text{isc}}k_r\), values are obtained for \(\Phi_{\text{isc}}k_r\) that do not exceed \(1.8 \times 10^2\) s\(^{-1}\) (Table 3.3). In fact, these values are much lower than that found e.g. for the isostructural complex \([\text{Ru(Cl)(Me)(CO)}_2(i\text{Pr-DAB})]\) (\(\Phi_{\text{isc}}k_r = 11 \times 10^2\) s\(^{-1}\)) having a lowest 3MLCT excited state. In general, 3MLCT states have radiative decay constants \(k_r\) that are even higher and range between \(10^4\) and \(10^5\). These low values of \(\Phi_{\text{isc}}k_r\) for the emission from the 3SBLCT state are rather unexpected since the electronic transition to the corresponding 1SBLCT state is strongly allowed (\(\varepsilon = 3 - 15 \times 10^3\) M\(^{-1}\).cm\(^{-1}\), Table 3.1), which implies a large \(k_r\). Hence \(\Phi_{\text{isc}}\) must be much smaller than unity resulting in a low value for \(\Phi_{\text{isc}}k_r\). Such values are obtained if crossing between 1SBLCT and 3SBLCT is slow or if there is a competing intersystem crossing from the 1SBLCT state to another, non-emitting, state of e.g. 3MLCT character. According to recent CASSCF/CASPT2 calculations of the ground and some singlet and triplet excited states of the model complex \([\text{Ru}(\text{SnH}_3)_2(CO)_2(\text{Me-DAB})]\), both factors may play an
important role here. Thus, the calculated energy difference between the $^1$SBLCT and $^3$SBLCT states of 5400 cm$^{-1}$ is rather high compared with that between the lowest $^1$MLCT and $^3$MLCT states (1500 cm$^{-1}$). This large energy difference may cause a slowing down of the intersystem crossing to such an extent that fluorescence from the $^1$SBLCT state can compete with this process. In fact a short-lived and only slightly Stokes-shifted emission was observed, most probably belonging to fluorescence from the $^1$SBLCT state.$^6,8$ This luminescence, which is not due to fluorescence from solvent impurities or any other artifact, has a lifetime of $8.0 \times 10^2$ ps for [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)] in a 2-MeTHF glass at 90 K. This lifetime was determined with a Hamamatsu streak camera setup,$^46$ using a nitrogen laser ($\lambda_{exc} = 337$ nm) as the excitation source.

A second noteworthy result of the CASSCF/CASPT2 calculations is the presence of a $^3$MLCT state very close in energy to the absorbing $^1$SBLCT state. Intersystem crossing to this $^3$MLCT state will compete with decay to the $^3$SBLCT state, the more since crossing between $^1$SBLCT and $^3$MLCT has been found to be much more efficient than between $^1$SBLCT and $^3$SBLCT states.$^47$ Moreover, occupation of the $^3$MLCT state in question is not expected to give rise to any strong additional emission since the electronic transition to the corresponding $^1$MLCT state, observed as a weak band at ca. 400 nm in the case of [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)], is overlap forbidden.

We therefore propose that the low emission quantum yields of the complexes under study are the result of two effects, i.e. the large energy gap between the $^1$SBLCT and $^3$SBLCT states and the presence of a non-emissive $^3$MLCT state close in energy to the $^1$SBLCT state.

### 3.6 Conclusions

The results of this study show that the photostability of these complexes at room temperature can be increased appreciably by using an $\alpha$-diimine with a low-lying $\pi^*$ orbital and osmium instead of ruthenium. In this way virtually photostable complexes were prepared with lifetimes of ca. 4 $\mu$s. In a glass at 80 K all complexes are photostable and since the complexes are only weakly distorted in their emitting $^3$SBLCT states according to the Stokes shift and resonance Raman spectra, extremely long emission lifetimes of up to 1.1 ms were obtained.
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The emission quantum yields are rather low and ab initio calculations suggest that this may be due to an inefficient decay to the emitting \(^3\text{SBLCT}\) state, but this will be investigated further by ultrafast time-resolved absorption studies.

3.7 References

Chapter 3. Tuning the Excited State Properties of \([M(SnR_3)_2(CO)_2(\alpha\text{-diimine})]\) (\(M = \text{Ru, Os}\))

The Excited-State and Redox Properties of 
\[ Ru(L_1)(L_2)(CO)_2(iPr-DAB) \] Complexes Bearing One or Two Electron Donating RuCp(CO)_2 Axial Ligands

4.1 Abstract

The photophysical, photochemical and redox properties of the title complexes were investigated. Resonance Raman measurements revealed the lowest-energy electronic transition to possess Sigma-Bond-to-Ligand Charge Transfer (SBLCT) character. At low temperatures long-lived near-IR emission was observed. Irradiation in solution results in homolytic splitting of a Ru–Ru bond as the primary step, followed by secondary reactions of the radical fragments depending on the experimental conditions. (Spectro)electrochemical investigations of the title species proved that the axial [RuCp(CO)₂] groups exert a stabilizing influence on the corresponding radical cations, while destabilizing the corresponding radical anions, compared to the redox behaviour of other ruthenium complexes of this type.

4.2 Introduction

The photochemical, photophysical and redox properties of the complexes trans, cis-[Ru(L₁)(L₂)(CO)₂(iPr-DAB)] (iPr-DAB = N,N-diisopropyl-1,4-diaza-1,3-butadiene) have been studied extensively in our laboratory.¹⁻⁵ In this general formula L₁ and L₂ represent electron donating ligands such as alkyl- or metal-containing groups. It was shown that in the lowest-excited state of these complexes electron density has been transferred from the σ(L₁–Ru–L₂) system to the π* orbital of iPr-DAB, which contrasts with the lowest MLCT state of [Ru(Cl)(Me)(CO)₂(iPr-DAB)] and the XLCT (X = I) state of [Ru(I)(Me)(CO)₂(iPr-DAB)].⁶⁻⁸ One of the consequences of this σπ* or Sigma-Bond-to-Ligand Charge Transfer (SBLCT) excited state character is a dramatic increase in excited state lifetime.² On the other hand, removal of electron density from the bonding L₁–Ru–L₂ σ orbital imparts all members of the series [Ru(L₁)(L₂)(CO)₂(iPr-DAB)] with a certain degree of photoreactivity.

The present study was undertaken to investigate the influence of strongly electron releasing axial ligands on the photophysical and photochemical behaviour. Therefore, two novel complexes were synthesized bearing one or two [RuCp(CO)₂] groups as axial ligands. It was expected that incorporation of these ligands would shift the electronic absorption maximum to lower energy, hence giving rise to near-infrared emission. This is very interesting in view of the challenging application of such compounds as luminescent labels.
e.g. in biochemical separations, since in the near infrared spectral region of the spectrum the background luminescence is negligible. A long luminescence lifetime is also desirable in order to make time gated detection viable. In order to understand the influence of the electron releasing \([\text{RuCp(CO)}_2]\) axial ligand(s) on the electronic properties and reactivity of the title complexes in more detail, a (spectro)electrochemical study was also undertaken.

4.3 Experimental Section

**Materials.** \([\text{Ru}_3(\text{CO})_{12}\) (ABCR), \(\text{I}_2\) (Merck), \(\text{SnClPh}_3\) (Aldrich) and \([\text{Ru(CO)}_2\text{Cp}]_2\) (Strem) were used as received. Solvents purchased from Acros (THF, 2-MeTHF, hexanes, dichloromethane), Merck (heptane) were dried on and distilled from the appropriate drying agent. Silica gel (kieselgel 60, Merck, 70–230 mesh) for column chromatography was dried and activated by heating in vacuo at 160 °C overnight.

**Syntheses.** All syntheses and measurements were performed under a nitrogen atmosphere using standard Schlenk techniques. \(\text{N,N'-disopropyl-1,4-diaza-1,3-butadiene (iPr-DAB),}^{26} [\text{RuCp(H)(CO)}_2]^{17} [\text{RuCp(CO)}_2]^2,^{17} [\text{Ru(Cl)(SnPh}_3)(\text{CO})_2(iPr-DAB)]^{10}\) and \([\text{Ru(I)}_2(\text{CO})_2(iPr-DAB)])^{27}\) were prepared according to literature procedures.

\([\text{Ru(SnPh}_3][\text{RuCp(CO)}_2](\text{CO})_2(iPr-DAB)]\) (1). \([\text{RuCp(CO)}_2]^2\) (216 mg, 0.48 mmol) was dissolved in 30 mL THF. An excess of 0.6 mL NaK was added through a syringe under stirring. The yellow colour of the reaction mixture changed to brown yellow during the next 45 min after which IR spectra showed virtually complete conversion to \([\text{RuCp(CO)}_2]^2\). The resulting solution was added gradually through a syringe to a solution of \([\text{Ru(Cl)(SnPh}_3)(\text{CO})_2(iPr-DAB)]\) (182 mg, 0.24 mmol) in 30 mL THF under the exclusion of light. The reaction mixture turned purple immediately. The solvent was evaporated and the product was purified by column chromatography on activated silica, using a \(\text{CH}_2\text{Cl}_2/\text{hexane} (1:3 \text{ v/v})\). The product elutes prior to the \([\text{RuCp(CO)}_2]^2\) main impurity. It was obtained as a purple microcrystalline solid in approximately 50% yield. FAB-MS; \(m/z: [M^+]\) not detected, 813 [M\(^+\) - 2 CO], 764 [M\(^+\) - Ph - CO], 649 [M\(^+\) - RuCp(CO)_2]. IR (THF): See Table 4.1. UV/Vis (\(\varepsilon/M^{-1}.cm^{-1}\)) (\(\text{CH}_2\text{Cl}_2\): See Table 4.1. \(^1\)H NMR (CDCl_3); \(\delta: 0.99\) (d, 6 H, \(^3J = 6.5\) Hz, CH(CH_2)_2 pointing toward SnPh_3, assignment based on comparison with the \(^1\)H NMR spectra of \([\text{Ru(SnPh}_3)_2(\text{CO})_2(iPr-DAB)]\) (\(\delta = 0.97\)\(^1\) and 2 (vide infra); 1.19 (d, 6 H, \(^3J = 6.5\) Hz, CH(CH_2)_2 pointing toward RuCp(CO)_2), 4.40 (septet, 2 H, \(^3J = 6.6\) Hz, CH(CH_2)_2), 5.22 (s, 5 H, C_3H_5), 7.27 (m, 9 H, \(\alpha/p-\text{SnC}_6\text{H}_5\)), 7.38 (m, 6 H, \(m-\text{SnC}_6\text{H}_5\)), 7.87 (s, 2 H, \(J_{\text{Sn-H}} = 21\) Hz, imine CH) ppm. \(^{13}\)C NMR APT (C_6D_6); \(\delta: 25.1, 24.5\) (CH(CH_3)_2), 63.0 (CH(CH_3)_2), 86.4 (C_3H_5), 128.0, 127.7 (s, m/p-\text{SnC}_6\text{H}_5).
137.8 (s, J_{Sn-C} = 34 Hz, o-SnC_6H_5), 144.5 (s, ipso-SnC_6H_5), 145.4 (s, imine C), 205.7 (s, Ru_{axial}-CO), 209.7 (s, Ru_{enantiomer}-CO) ppm. ^{119}Sn NMR (acetone-d_6): δ: -45.6 ppm.

[Ru[RuCp(CO)_{2}]_2(CO)(iPr-DAB)] (2). This compound was synthesized from [Ru(I)(CO)_{2}(iPr-DAB)] (104 mg, 0.19 mmol) following the same procedure as for 1 and obtained as a dark green microcrystalline solid in approximately 50% yield.

C_{24}H_{26}N_{2}O_{6}Ru_3 (869.52): calcd. C 38.87, H 3.53, N 3.78; found C 38.69, H 3.36, N 3.70. FAB-MS: m/z: 743 [M^+], 521 [M^+ - RuCp(CO)_{2}]. IR (THF): See Table 4.1. UV/Vis (ε/M^{-1}.cm^{-1}) (CH_2Cl_2): See Table 4.1. ^1H NMR (CDCl_3): δ: 1.21 (d, 12 H, J = 6.6 Hz, CH(CH_3)_2), 4.36 (sept, 2 H, J = 6.6 Hz, CH(CH_3)_2), 5.24 (s, 10 H, C_5H_5), 7.99 (s, 2H, imine CH) ppm. ^13C NMR AP T (C_6D_6): δ: 24.8 (CH(CH_3)_2), 61.6 (CH(CH_3)_2), 86.4 (C_5H_5), 143.7 (imine C), 205.7 (Ru_{axial}-CO), 214.6 (Ru_{enantiomer}-CO) ppm.

**Spectroscopic Measurements.** UV/Vis: Varian Cary 4E and Hewlett-Packard 8453. IR: Bio-Rad FTS 7 and FTS 60A, the latter equipped with a liquid-nitrogen-cooled MCT detector. NMR: Bruker AMX300 (^1H and ^13C) and DRX300 (^119Sn). Resonance Raman: Dilor XY spectrometer, with an SP2040E Ar^+ laser and Coherent CR 490 and 590 dye lasers as excitation sources and a Wright Instruments CCD detector. EPR: Varian E-104A. FAB-MS: JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system. Elemental analyses were performed at H. Kolbe Mikroanalytisches Laboratorium in Mülheim an der Ruhr.

Time-resolved emission and absorption spectra were recorded at 90 K in an Oxford Instruments cryostat. A Spectra Physics GCR-3 Nd:YAG laser, operating at 10 Hz was used as the excitation source. The desired wavelength (532 nm) was obtained by frequency doubling of the 1064 nm fundamental. The setup has been described elsewhere. For the low temperature absorption, a teflon mask with 1 mm holes for the probe light and a 1 cm slit for the pump light was used.

Quantum yields of the photoreactions were determined from the disappearance of the parent complexes, following the decay of their lowest-energy absorption band. For this purpose the sample was irradiated within the UV/Vis spectrophotometer with one of the laser lines of an SP2025 Ar^+ laser through an optical fiber in a previously described setup.

Cyclic Voltammograms (CV) of approximately 10^{-3} M solutions of the parent complexes were recorded with added NBu_4PF_6 (0.1 - 0.3 M) as supporting electrolyte in a gas-tight, single-compartment, three-electrode cell equipped with platinum disk working (apparent surface area 0.42 mm^2), platinum gauze auxiliary and silver wire pseudoreference electrodes. The cell was connected to a computer-controlled PAR Model 283 potentiostat. Redox potentials are reported relative to E_0(Fc/Fc^+) (E_0 = 0.575 and 0.43 V vs SCE in THF and CH_2CN, respectively). Ferrocene was added as internal standard. The scan speed was 100 mV/s. IR-spectroelectrochemical measurements at variable temperatures were performed with ca. 10^{-2} M solutions in previously described optically transparent thin-layer electrochemical (OTTLE) cells. The potential was controlled during these measurements by a PA4 (EKOM, Czech Republic) potentiostat.
4.4 Results and Discussion

4.4.1 Spectroscopic Properties

The title compounds, purple [Ru(SnPh₃){Ru(Cp(CO)₂)(CO)(iPr-DAB)}] 1 and green [Ru{Ru(Cp(CO)₂)(CO)(iPr-DAB)}] 2 were prepared by addition of K[Ru(Cp(CO)₂)] to [Ru(Cl)(SnPh₃)(CO)₂(iPr-DAB)] and [Ru(I)₂(CO)₂(iPr-DAB)] respectively, according to the procedure used for the synthesis of [Ru(Re(CO)₃)(CO)(iPr-DAB)]. Both complexes are highly photoreactive in solution and virtually photostable in the solid state. The ¹H and ¹³C NMR chemical shifts for the coordinated iPr–DAB ligand are similar to those found for other trans, cis-[Ru(L₁)(L₂)(CO)₂(iPr–DAB)] complexes, pointing to axial positions of the [Ru(Cp(CO)₂)] groups (See Figure 4.1). Both 1 and 2 may exist as a mixture of several rotamers in solution.

![Figure 4.1 Schematic molecular structures of the complexes 1 and 2.](image)

The electronic absorption data are collected in Table 4.1. Due to the electron-releasing character of the [RuCp(CO)₂] group, the lowest-energy absorption bands of both 1 and 2 are red-shifted compared to those of other complexes of this series such as [Ru(SnPh₃)₂(CO)₂(iPr–DAB)]. In the case of 1 this absorption band is considerably less solvatochromic than e.g. the Metal-to-Ligand Charge Transfer (MLCT) band of the structurally related complex [Ru(Cl)(Me)(CO)₂(iPr–DAB)] and even less than found for all presently known non-halide complexes of the [Ru(L₁)(L₂)(CO)₂(iPr–DAB)] series. For 2 the solvatochromism is negligible. This is indicative of an electronic transition with a limited charge transfer character. Upon cooling a 2-MeTHF solution of 1 or 2 to a glassy solid at 80 K the lowest-energy band shifts to higher energy by ca. 350 cm⁻¹.
Chapter 4. Excited State and Redox Properties of Complexes Bearing RuCp(CO)$_2$ ligands

Table 4.1 Spectroscopic data for complexes 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>UV/Vis$^a$</th>
<th>IR$^c$</th>
<th>resonance Raman (cm$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>$\lambda_{\text{max}}$ (e$^-$)</td>
<td>$\Delta^d$</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>571(5770),383,333,306</td>
<td>368</td>
<td>1993s,1960s,1933s, 1460s,1281s,951s,829s,609m,416w,242m,192m</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1918w</td>
</tr>
<tr>
<td>2</td>
<td>605(7070),463,352</td>
<td>82</td>
<td>1991w,1967s,1946s, 1459vw,1281vw,954m,833m,601m,499w,320s,</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1926s,1919sh,1897w 184s,119s,104s</td>
</tr>
</tbody>
</table>

$^a$in CH$_2$Cl$_2$ at room temperature, $^b$in nm, $^c$in M$^{-1}$cm$^{-1}$, $^d\Delta = \nu_{\text{max}}$(MeCN) $- \nu_{\text{max}}$(hexane) (in cm$^{-1}$); $^e$in THF at room temperature.

In order to characterize the lowest-energy electronic transition, resonance Raman (rR) spectra were recorded for both complexes by irradiation into the corresponding absorption band. This technique relies on the resonance enhancement of Raman intensity for those vibrations which are coupled to the allowed electronic transition activated by laser excitation. The wavenumbers of the observed Raman bands are collected in Table 4.1. The rR spectra of 1 and 2 (Figure 4.2) are significantly different. That of 1 shows resonantly enhanced Raman bands at 1460 cm$^{-1}$ and 1281 cm$^{-1}$, which belong to $\nu_6$(CN) and $\delta$(CH) of the coordinated iPr–DAB ligand, respectively.$^2$ Their resonance enhancement indicates that the electronic transition involves some degree of charge transfer to the lowest $\pi^*$ orbital of the iPr–DAB ligand. Its occupation gives rise to a lengthening of the C=N bond and appearance of the corresponding stretching mode in the rR spectrum. The absence of a resonantly enhanced $\nu_6$(CO) band implies that the $\pi$-backbonding from the central Ru atom to the CO ligands is similar in ground and excited states, which agrees with a delocalized Ru–Ru(iPr–DAB)–Sn system and a small charge transfer character of the transition. In contrast, rR spectra obtained by excitation into MLCT transitions, for example in the case of [Ru(Cl)(Me)(CO)$_2$,(iPr–DAB)]$,^6$ show a rR effect for $\nu_6$(CO)$^6$, in agreement with their pronounced MLCT character. In the case of 2 the lowest-energy transition has virtually no charge transfer character since the bands due to the internal stretching vibrations of the iPr–DAB ligand are absent in the rR spectrum. This observation is in line with the negligible solvatochromism of this absorption band. This effect of the charge transfer character on the resonance Raman spectrum is not a particular property of an SBLCT transition; it has also been found for the MLCT transitions of W(CO)$_4$(α-diimine) (see chapter 8).$^{11}$
Based on the rR data, the lowest-energy absorption band of 1 is assigned to an electronic transition qualitatively described as $\sigma$(Sn–Ru–Ru)$\rightarrow$$\pi^{*}$(iPr–DAB) (SBLCT) with some mixing between the $\sigma$ and $\pi^{*}$ orbitals. In the case of 2 this transition occurs between frontier orbitals possessing a strongly mixed $\sigma$(Ru–Ru–Ru)$\rightarrow$$\pi^{*}$(iPr–DAB) character. A similar mixing between $\sigma$ and $\pi^{*}$ orbitals was found in density functional calculations on the related model compound $[\text{Ru(SnH}_{3}\text{]}_{2}(\text{CO})_{2}(\text{H–DAB})]$. These calculations described the HOMO and LUMO as mixed contributions of a Ru p orbital, the sp$^{3}$–sp$^{3}$ combination of the SnH$_{3}$ ligands and the $\pi^{*}$(H–DAB) orbital. The contribution of the $\pi^{*}$(iPr–DAB) orbital to the HOMO and LUMO is expected to vary from one complex to another, with a concomitant effect on the charge transfer character and the solvatochromism of the HOMO$\rightarrow$LUMO (SBLCT) transition.

![Resonance Raman spectra of 1 (top) and 2 (bottom) recorded by excitation ($\lambda_{\text{exc}}$ = 514.5 and 590.0 nm, respectively, indicated by arrows) into the lowest-energy transition (UV/Vis spectra in inserts) of the complexes dispersed in KNO$_{3}$-pellets.](image)

**Figure 4.2** Resonance Raman spectra of 1 (top) and 2 (bottom) recorded by excitation ($\lambda_{\text{exc}}$ = 514.5 and 590.0 nm, respectively, indicated by arrows) into the lowest-energy transition (UV/Vis spectra in inserts) of the complexes dispersed in KNO$_{3}$-pellets.

Going from 1 to 2, i.e. replacing the axial SnPh$_{3}$-ligand by the more electron releasing [RuCp(CO)$_{2}$] group, the mixing between the $\sigma$ and $\pi^{*}$ orbitals in both the HOMO and the LUMO increases. As a result the HOMO$\rightarrow$LUMO transition loses most of its charge transfer
character, which is reflected in the absence of bands due to the iPr–DAB stretching vibrations in the rR spectrum of 2. In the 1000 – 100 cm$^{-1}$ region of the rR spectrum of 1 resonantly enhanced bands can be observed at 951 and 829 cm$^{-1}$ (iPr–DAB deformation vibrations) and at 609, 416, 242 and 192 cm$^{-1}$ (metal–ligand stretching modes). These bands were also observed in the rR spectra of [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)] and [Ru(SnPh$_3$){Mn(CO)$_5$}(CO)$_2$(iPr–DAB)]. In addition to these vibrations, the rR spectrum of 2 shows extra bands at 499, 320, 119 and 104 cm$^{-1}$, while the peak at 242 cm$^{-1}$ is missing. The latter two bands are very intense and may belong to a $\nu$(Ru–Ru) or a $\nu$(Ru–Ru–Ru) mode.

Table 4.2 Emission properties of compounds 1 and 2 in a 2-MeTHF glass at 80 K ($\lambda_{\text{ex}}$ = 532 nm).

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$\tau$ (\mus)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>559</td>
<td>830</td>
<td>5841</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>593</td>
<td>855</td>
<td>5168</td>
<td>9</td>
</tr>
<tr>
<td>Ru(Cl)(Me)(CO)$_2$(iPrDAB)$^a$</td>
<td>387</td>
<td>650</td>
<td>10455</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$^a$from ref$^7$.

Figure 4.3 Low temperature transient absorption difference spectra of 1 (top) and 2 (bottom) in 2-MeTHF glasses at 90K. The time delay between spectra is 4 \us.
4.4.2 Low Temperature Emission and Transient Absorption

In a 2-MeTHF glass at 80 K both 1 and 2 show luminescence with a much longer lifetime than that of [Ru(Cl)(Me)(CO)2(iPr-DAB)] (Table 4.2). This is remarkable, since 1 and 2 emit in the near infrared region, whereas the latter compound emits at much higher energy. At first sight, this observation seems to be in contradiction with the energy gap law. However, it can be explained by the fact that the lowest excited state has a different character. As mentioned in the section 4.1 and chapter 1, the use of two σ-bound axial donor ligands results in a special type of lowest excited state, the SBLCT state. The long excited state lifetime is a general property of this type of excited state, and can be rationalized as follows: In the SBLCT excited state the complexes are less distorted, which is reflected in a smaller apparent Stokes shift of their emission (Table 4.2). This feature originates in the delocalized nature of the electronic system, causing a slight distortion of many bonds in the excited state, while the distortion along any normal coordinate is very small. Consequently, the excited state lifetime increases, owing to reduction of vibrational overlap between ground and excited state wavefunctions. This situation also applies to related [Ru(L1)(L2)(CO)2(iPr-DAB)] complexes, as judged from time-resolved emission and infrared data and from MO calculations. At low temperatures, it proved possible to record transient absorption spectra as well (Figure 4.3). The transient features and ground state bleach have the same lifetime as found in the emission spectra. Interestingly, the bleach does not disappear completely, indicating a slight photolability of 1 and 2 even in low temperature glasses.

4.4.3 Photochemistry

Complexes 1 and 2 are photoreactive in solution upon irradiation into their lowest SBLCT absorption band. The photoreactions were monitored with UV/Vis, IR and EPR spectroscopies. The spectroscopic data of the parent complexes, photoproducts and reference compounds are collected in Table 4.3 and the photoreaction pathways are summarized in Scheme 4.1.

First of all, solutions of 1 and 2 were irradiated in situ in an EPR spectrometer in the presence of a radical trap. The EPR spectrum recorded after irradiation of a THF solution of 1 in the presence of an excess of triphenylphosphine with a high-pressure mercury lamp (λ>455 nm) was identical to that of the radical [Ru(SnPh3)(PPh3)(CO)2(iPr-DAB)]*, obtained by irradiation of [Ru(SnPh3)2(CO)2(iPr-DAB)] in the presence of triphenylphosphine. The other radical fragment, [RuCp(CO)2]*, which was also formed by
the homolysis of the Ru–Ru bond, was not observed. However, on irradiation of 1 in toluene containing an excess of nitrosodurene, a different radical species was formed, which was identified as the nitrosodurene-trapped [RuCp(CO)]* radical.\(^\text{12}\) Exactly the same spectrum was recorded upon irradiation of 2 under the same conditions, proving that in both cases homolytic Ru–Ru bond splitting is the primary photochemical process.

In situ laser irradiation (\(\lambda_{\text{irr}} = 514.5\) nm) of 1 in dichloromethane in an IR spectrometer at room temperature caused the appearance of several new bands in the CO stretching region, while those of the starting compound decreased in intensity. Initially, two bands appeared at 2056 and 2005 cm\(^{-1}\), accompanied by three other bands at 1991, 1965 and 1936 cm\(^{-1}\). The former two bands are assigned to [RuCp(Cl)(CO)]\(_2\), in good agreement with the literature values of 2057 and 2009 cm\(^{-1}\) in CCl\(_4\).\(^\text{13}\) The other three bands are attributed to [Ru(SnPh\(_3\))(CO)]\(_2\)(iPr-DAB)]\(_2\), a product which also results from photolysis of [Ru(SnPh\(_3\))\(_2\)(CO)]\(_2\)(iPr-DAB)].\(^\text{33}\) In addition, a small peak is detectable at 1773 cm\(^{-1}\), which is assigned to [RuCp(CO)]\(_2\), its other v(CO) bands being obscured by the previously mentioned bands.

![Figure 4.4 UV/Vis spectral changes accompanying 514.5 nm irradiation of 2 in THF at room temperature.](image)
### Table 4.3 Spectroscopic data of complexes 1 and 2 and their photoproducts upon 514.5 nm irradiation.

<table>
<thead>
<tr>
<th>Compound (solvent/temp)</th>
<th>( v(\text{CO}) ) (cm(^{-1}))</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (CH(_2)Cl(_2); 293 K)</td>
<td>1993m, 1961s, 1933s, 1920sh</td>
<td>308, 334, 384, 571</td>
</tr>
<tr>
<td>[Ru(Cp)(Cl)(CO)](_2)</td>
<td>2056, 2005</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cl)(SnPh(_3))(CO)(_2)(iPrDAB)]</td>
<td>2032, 1974</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(SnPh(_3))(CO)(_2)(iPrDAB)](_2)</td>
<td>1991w, 1965m, 1936s</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(CO)(_2)]</td>
<td>1773(^a)</td>
<td>-</td>
</tr>
<tr>
<td>1 (THF; 213 K)</td>
<td>1991m, 1958s, 1931s, 1915w</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(THF)(CO)(_2)](^*)</td>
<td>2045, 1991</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(H)(CO)(_2)]</td>
<td>2026, 1959</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(SnPh(_3))(CO)(_2)(iPrDAB)](_2)</td>
<td>1991w, 1959m, 1932s</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(CO)(_2)]</td>
<td>1991, 1776(^a)</td>
<td>-</td>
</tr>
<tr>
<td>1 (THF; 293 K)</td>
<td>1993m, 1960s, 1933s, 1918w</td>
<td>308, 333, 382, 570</td>
</tr>
<tr>
<td>unassigned</td>
<td>2037, 2010</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(H)(CO)(_2)]</td>
<td>2022, 1961</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(SnPh(_3))(CO)(_2)(iPrDAB)](_2)</td>
<td>1991w, 1961m, 1935s</td>
<td>385, 690</td>
</tr>
<tr>
<td>[Ru(Cp)(CO)(_2)]</td>
<td>1991, 1961, 1935, 1783</td>
<td>-</td>
</tr>
<tr>
<td>2 (CCl(_4); 263 K)</td>
<td>1996w, 1971s, 1948s, 1929s, 1922sh, 1898w</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(Cl)(CO)(_2)]</td>
<td>2058, 2009</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cl)(Ru(Cp)(CO)(_2))(CO)(_2)(iPrDAB))]</td>
<td>1974s, 1953m, 1923w, 1767w</td>
<td>-</td>
</tr>
<tr>
<td>2 (THF; 213 K)</td>
<td>1990w, 1965s, 1945s, 1924s, 1894w</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Cp)(THF)(CO)(_2)](^*)</td>
<td>2045, 1990</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Ru(Cp)(CO)(_2))(THF)(CO)(_2)(iPrDAB)](^*)</td>
<td>1967s, 1943m, 1924w, 1763w</td>
<td>-</td>
</tr>
<tr>
<td>2 (THF; 293 K)</td>
<td>1992w, 1967s, 1946s, 1926s, 1919sh, 1897w</td>
<td>350, 462, 604</td>
</tr>
<tr>
<td>[Ru(Cp)(H)(CO)(_2)]</td>
<td>2023, 1959</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Ru(Cp)(CO)(_2))(THF)(CO)(_2)(iPrDAB)](^*)</td>
<td>1972s, 1959m, 1925w, 1764w</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(Ru(Cp)(CO)(_2))(CO)(_2)(iPrDAB)](_2)</td>
<td>1988, 1959, 1940</td>
<td>495, 703</td>
</tr>
</tbody>
</table>

**Reference compounds**

| [Ru(SnPh\(_3\))(CO)\(_2\)(iPrDAB)](THF)\(^b\) | 1988w, 1963m, 1934s | 385, 690 |
| [Ru(OtBu)(SnPh\(_3\))(CO)\(_2\)(iPrDAB)](THF)\(^b\) | 2040, 1981 | - |
| [Ru(Cp)(CO)\(_2\)](THF) | 2009w, 1997s, 1967m, 1955m, 1936s, 178 | 265, 331 |
| 3s | - | - |
| [Ru(Cp)(CO)\(_2\)](THF; 213 K) | 1992s, 1965w, 1948w, 1934w, 1778s | - |
| [Ru(Cp)(CO)\(_2\)](CH\(_2\)Cl\(_2\)) | 2002s, 1966s, 1936m, 1773s | - |
| [Ru(Cp)(H)(CO)\(_2\)] (Heptane)\(^e\) | 2032, 1974 | - |
| [Ru(Cp)(H)(CO)\(_2\)](THF) | 2022, 1960 | - |
| [Ru(Cp)(H)(CO)\(_2\)](CH\(_2\)Cl\(_2\)) | 2025, 1953 | - |
| [Ru(Cp)(Cl)(CO)\(_2\)](CCl\(_4\))\(^d\) | 2057, 2009 | - |
| [Ru(Cp)(THF)(CO)\(_2\)]\(^*\) | 2048, 1995 | - |
| [Ru(Cl)(SnPh\(_3\))(CO)\(_2\)(iPrDAB)] | 2033, 1974 | - |

\(^a\)The other \( v(\text{CO}) \) bands are obscured by those of the other photoproducts; \(^b\)ref \(^3\); \(^c\)ref 17; \(^d\)ref 13; 
\(^e\)with added NBu\(_4\)PF\(_6\) electrolyte.
On prolonged irradiation of the dichloromethane solution of 1 new bands appeared at 2033 and 1974 cm\(^{-1}\) at the expense of the peaks belonging to [Ru(SnPh\(_3\))(CO)\(_2\)(iPr-DAB)]\(_2\). These IR peaks and an absorption band at ca. 440 nm reveal the formation of [Ru(Cl)(SnPh\(_3\))(CO)\(_2\)(iPr-DAB)] in agreement with literature data for this complex.\(^3\) The dichloromethane solvent apparently does not act as an efficient radical scavenger, allowing the [Ru(SnPh\(_3\))(CO)\(_2\)(iPr-DAB)]\(^*\) and [RuCp(CO)\(_2\)]\(^*\) radicals to dimerize before chlorine abstraction from the solvent takes place. This particularly applies to the former radical. The photochemical quantum yield of this reaction was determined and appeared to be rather high (0.71). These data show that SBLCT excitation of 1 causes homolysis of the Ru–Ru bond, followed by dimerization or reaction with the solvent (Scheme 4.1). The Ru–Sn bond remains unaffected.

Irradiation (\(\lambda_{irr} = 514.5\) nm) of 2 in spin trapping CCl\(_4\) at 263 K gave rise to several new \(\nu(CO)\) bands belonging to two chlorinated products (Scheme 1). The bands at 2058 and 2009 cm\(^{-1}\) belong to [RuCp(Cl)(CO)\(_2\)] in agreement with literature data.\(^13\) The second product (\(\nu(CO)\) at 1974, 1953, 1923 and 1767 cm\(^{-1}\)) is assigned to [Ru(Cl)[RuCp(CO)\(_2\)](CO)\(_2\)(iPr-DAB)]. The interesting feature of this product is the \(\nu(CO)\) band due to a bridging carbonyl group (1767 cm\(^{-1}\)). We assume that one carbonyl group occupies a Ru–Ru bridging position. The quantum yield of the photochemical reaction of 2 was determined to be 1.16 in CH\(_2\)Cl\(_2\). This quantum yield, and also that for 1 (see above), is much higher than that for [Ru(SnPh\(_3\))(CO)\(_2\)(iPr-DAB)] (0.10, chapter 3), which implies that the Ru–Ru bond is weaker than the Ru–Sn bond. The quantum efficiency higher than 1 may indicate that the radicals, formed upon homolytic Ru–Ru bond splitting, react with the starting compound in an electron transfer chain reaction. Similar observations were made for several related rhenium, manganese and ruthenium complexes.\(^14\)–\(^16\)

For comparison, the photochemistry of 1 and 2 was also studied in THF in the absence of radical traps (Scheme 4.1). In this case the major photoproduct of 1 was clearly [Ru(SnPh\(_3\))(CO)\(_2\)(iPr-DAB)]\(_2\) (\(\nu(CO) = 1991, 1961, 1935\) cm\(^{-1}\), \(\lambda_{max} = 385, 690\) nm). The other expected dimeric product [RuCp(CO)\(_2\)]\(_2\) was only formed in a minor amount. In addition, some other bands were observed at 2037, 2022 and 2010 cm\(^{-1}\). These peaks increased in intensity on prolonged irradiation, at the expense of those belonging to [RuCp(CO)\(_2\)]\(_2\). The band at 2022 cm\(^{-1}\), together with a band at \(\sim 1960\) cm\(^{-1}\) (hidden under the 1961 cm\(^{-1}\) band), is assigned to [RuCp(H)(CO)\(_2\)], formed via hydrogen abstraction from the solvent by [RuCp(CO)\(_2\)]\(^*\). The same \(\nu(CO)\) values were found for [RuCp(H)(CO)\(_2\)]
synthesized from \( \text{Ru}_3(\text{CO})_{12} \) and cyclopentadiene.\(^{17}\) Similar reactions of \([\text{RuCp}(\text{CO})_2]^+\) were reported recently.\(^{18}\) The assignment of the 2037 and 2010 cm\(^{-1}\) bands is not entirely clear, but they must also belong to a species containing the \([\text{RuCp}(\text{CO})_2]\) moiety. On irradiation at 213 K in THF the major products were the same. However the 2037 and 2010 cm\(^{-1}\) bands were absent, whereas a new product was observed with bands at 2045 and 1991 cm\(^{-1}\), fitting nicely with data for the \([\text{RuCp}((\text{THF})(\text{CO})_2)]^+\) cation (Table 4.3).

\[
\begin{align*}
\text{[Ru(SnPh}_3)(\text{CO})_2(iPr-DAB)]^+ & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru(SnPh}_3)(\text{CO})_2(iPr-DAB)]_2 & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru(Cl)(SnPh}_3)(\text{CO})_2(iPr-DAB)] & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru(THF)(SnPh}_3)(\text{CO})_2(iPr-DAB)] & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{[Ru(Pr)(SnPh}_3)(\text{CO})_2(iPr-DAB)] & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru(H)(SnPh}_3)(\text{CO})_2(iPr-DAB)] & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru(Cl)(SnPh}_3)(\text{CO})_2(iPr-DAB)] & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{[Ru{(RuCp(CO)}_2)(\text{CO})_2(iPr-DAB)]^+} & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru{(RuCp(CO)}_2)(\text{THF})(\text{CO})_2(iPr-DAB)]^+} & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\text{[Ru{(RuCp(CO)}_2)(\text{Cl})(\text{CO})_2(iPr-DAB)]} & \rightarrow [\text{RuCp}(\text{CO})_2]^+ \\
\end{align*}
\]

Scheme 4.1 Photochemical pathways of 1 and 2 in various solvents.
Irradiation of a THF solution of 2 also yielded a mixture of products. Clearly visible are peaks at 2023 and ~1960 cm\(^{-1}\) due to [RuCp(H)(CO)]\(_2\). In addition, there is a series of peaks at 1967, 1943, 1924 and 1766 cm\(^{-1}\), which most probably belong to [Ru{RuCp(CO)}\(_2\)](THF)(CO)]\(_2\)(iPr–DAB)]\(^+\), in close correspondence with the \(\nu\)(CO) values for the chlorinated derivative formed in CCl\(_4\) (vide supra). A third product with \(\nu\)(CO) bands at 1988, ~1960 and 1940 cm\(^{-1}\) is proposed to be [Ru{RuCp(CO)}\(_2\)](CO)]\(_2\)(iPr–DAB)]\(_2\). This assignment is not only in agreement with the behaviour of 1, but is also supported by the investigation of this reaction with UV/Vis spectroscopy. The product spectrum exhibits a low energy absorption band at 703 nm which is characteristic for such a dimer (Figure 4.4).\(^3\) At low temperatures (213 K) no dimeric products were observed, but only the cationic species [Ru{RuCp(CO)}\(_2\)](THF)(CO)]\(_2\)(iPr–DAB)]\(^+\) and [RuCp(THF)(CO)]\(_2\)]\(^+\). Apparently, the increased viscosity of the solvent at low temperatures hampers the dimerization of the radicals, while coordination of THF induces electron transfer reactions.

![Figure 4.5 Cyclic voltammograms showing the oxidation of 1 (A) and 2 (C) and the reduction of 1 (B) and 2 (D) in butyronitrile solutions at 213 K.](image)

**4.4.4 Redox properties and reactivity**

The complexes 1 and 2 were the subject of a (spectro)electrochemical study. Cyclic voltammograms were recorded at variable temperatures to determine the electrode potentials
and to study the reversibility of the corresponding redox processes (Figure 4.5, Table 4.4). The nature of the redox products was investigated by IR-spectroelectrochemistry. The spectroscopic data are collected in Table 4.5.

**Table 4.4 Reduction and oxidation potentials (V vs Fc/Fc\textsuperscript{+})**

<table>
<thead>
<tr>
<th>compound</th>
<th>(E_{p,a})</th>
<th>(E_{p,c})</th>
<th>(\Delta E_p^a)</th>
<th>conditions</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-1.98)</td>
<td>0.16</td>
<td>0.00</td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>1</td>
<td>(-1.89^b)</td>
<td>0.17</td>
<td>0.07</td>
<td>nPrCN/213 K</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>(-2.04)</td>
<td>0.06</td>
<td>0.06</td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>(-2.11)</td>
<td>(-0.09)</td>
<td>0.06</td>
<td>nPrCN/213 K</td>
<td>this work</td>
</tr>
<tr>
<td>[Ru<a href="CO">RuCp(CO)\textsubscript{2}</a>\textsubscript{2}(iPrDAB)]\textsuperscript{+}</td>
<td>(-1.47)</td>
<td>0.24</td>
<td></td>
<td>nPrCN/213 K</td>
<td>this work</td>
</tr>
<tr>
<td>[RuCp(CO)\textsubscript{2}]\textsuperscript{2}</td>
<td>(-2.57)</td>
<td>0.37</td>
<td></td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>[RuCp(THF)(CO)\textsubscript{2}]\textsuperscript{+}</td>
<td>(-1.47)</td>
<td>(-1.27)</td>
<td></td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>[RuCp(CO)\textsubscript{2}]\textsuperscript{2}</td>
<td>(-1.91)</td>
<td>0.34</td>
<td></td>
<td>THF/293 K</td>
<td>5</td>
</tr>
<tr>
<td>[Ru(SnPh\textsubscript{3})(CO)\textsubscript{2}(iPrDAB)]</td>
<td>(-1.91)</td>
<td>(-1.07)</td>
<td></td>
<td>THF/293 K</td>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\)anodic process, \(\Delta E_{p}(Fc/Fc^+)=0.06\) V; \(^b\)\(\Delta E_p=0.12\) V; \(^c\)the redox behaviour of the dimer [RuCp(CO)\textsubscript{2}]\textsuperscript{2} in THF was studied independently by cyclic voltammetry and IR spectroelectrochemistry. Literature data in refs \(^{31,32}\).

At room temperature the oxidation of 1 is chemically completely irreversible in THF. However, at 213 K in butyronitrile two oxidation waves became apparent, with the first oxidation process (O1) being partly reversible (\(I_a/I_a=0.7\)) on the voltammetric timescale at the scan rate of 100 mV/s (Figure 4.5A). The following anodic step (O2) is completely irreversible. The fact that the step O1 was found more than 150 mV more negatively than that of [Ru(SnPh\textsubscript{3})(CO)\textsubscript{2}(iPr-DAB)]\textsuperscript{5} indicates that the oxidation of 1 is significantly located on the [RuCp(CO)\textsubscript{2}] moiety.

Oxidizing 1 at O1 led to the appearance of four bands in the IR carbonyl-stretching region. The product formation was independent of the temperature employed. The primary one-electron oxidized product detected at RR1 (Figure 4.5A) at 213 K by cyclic voltammetry, is not detectable on the spectroelectrochemical timescale of seconds to minutes. Of the four bands, those at 2079 and \(-2030\) cm\textsuperscript{-1} are attributed to [RuCp(nPrCN)(CO)\textsubscript{2}]\textsuperscript{+}, in accordance with both the literature values of 2090 and 2044 cm\textsuperscript{-1} for [RuCp(MeCN)(CO)\textsubscript{2}]\textsuperscript{+} in CH\textsubscript{2}Cl\textsubscript{2} \(^{19}\) and with the observation that upon electrochemical oxidation of [RuCp(CO)\textsubscript{2}]\textsubscript{2} in nPrCN a product with identical \(\nu(CO)\) wavenumbers was formed (Table 4.5). The two remaining
bands (2042 and 1987 cm\(^{-1}\)) must be due to \([\text{Ru(SnPh}_3\text{(nPrCN)}(\text{CO})_2(\text{iPr-DAB})]^+\), as their wavenumbers are close to the values found for \([\text{Ru(OTf)}(\text{SnPh}_3)(\text{CO})_2(\text{iPr-DAB})]\) (2040 and 1981 cm\(^{-1}\) in THF).\(^\text{10}\) Taking these data into account, we propose the following oxidation path for 1: initially, the unstable radical cation (1\(^{**}\)) is formed, which rapidly splits to give the five-coordinate \([\text{Ru(SnPh}_3)(\text{CO})_2(\text{iPr-DAB})]^+\) radical and the \([\text{RuCp(nPrCN)}(\text{CO})_2]^+\) cation. The former species binds a solvent molecule and converts to the corresponding cation in a second oxidation step. On the reverse scan, small cathodic peaks were observed (RR2, Figure 4.5A), but the corresponding processes were not investigated in detail.

### Table 4.5 IR-spectroelectrochemical data of reduction (THF, room temperature) and oxidation (nPrCN, 193 K) products.

<table>
<thead>
<tr>
<th>compound</th>
<th>v(CO) (cm(^{-1}))</th>
<th>conditions</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1992m, 1958s, 1930s, 1913w</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>1992m, 1969s, 1932s, 1916w</td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>1989w, 1965s, 1946s, 1924s, 1910sh</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>1992w, 1967s, 1946s, 1926s, 1915sh</td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>1992w, 1967s, 1946s, 1926s, 1915sh</td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>[RuCp(nPrCN)(CO)_2]^+</td>
<td>2079, 2031</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
<tr>
<td>[RuCp(MeCN)(CO)_2]^+</td>
<td>2090, 2044</td>
<td>CH_2Cl_2/293 K</td>
<td>19</td>
</tr>
<tr>
<td>[RuCp(CO)_2]^+</td>
<td>1887, 1801</td>
<td>THF/293 K</td>
<td>this work</td>
</tr>
<tr>
<td>[Ru(SnPh)_3(nPrCN)(CO)_2(iPrDAB)]^+</td>
<td>2041, 1987</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
<tr>
<td>[Ru(SnPh)_3(OTf)(CO)_2(iPrDAB)]</td>
<td>2040, 1981</td>
<td>THF/293 K</td>
<td>10</td>
</tr>
<tr>
<td>[Ru(SnPh)_3(CO)_2(iPrDAB)]^-</td>
<td>1924, 1856</td>
<td>THF/293 K</td>
<td>5</td>
</tr>
<tr>
<td>[Ru<a href="CO">RuCp(CO)_2</a>_2(iPrDAB)]^{**}</td>
<td>2021w, 1997s, 1981s, 1962s, 1930w</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
<tr>
<td><a href="iPrDAB">Ru(nPrCN)(CO)_2</a>]^{2+}</td>
<td>2116, 2060s h</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
<tr>
<td>[Ru{RuCp(CO)_2}(CO)_2(iPrDAB)]^-</td>
<td>1927, 1847</td>
<td>nPrCN/193 K</td>
<td>this work</td>
</tr>
</tbody>
</table>

The oxidation of 2 is completely irreversible in THF at room temperature. However, at 213 K in butyronitrile at a \(v \geq 100\) mV/s the first oxidation process (O1) is completely reversible, as indicated by \(\Delta E_p = 61\) mV and \(I_c/I_a = 1\) (Figure 4.5C). For equimolar solutions of 1 and 2 virtually the same anodic current was observed at \(E_a(01)\) at 213 K. Considering similar values for the diffusion coefficients of 1 and 2, this reveals that also the oxidation of 2 at low temperatures is a one-electron process. Indeed, the initial oxidation product of 2 observed in the corresponding IR-spectroelectrochemical experiment in nPrCN at 193 K
exhibits a $\nu$(CO) pattern very close to that of the parent compound 2, but shifted by ca. 35 cm$^{-1}$ to larger wavenumbers ($\nu$(CO) at 2021, 1997, 1981, 1962 and 1930 cm$^{-1}$, Figure 4.6). This points to a similar molecular structure of the one-electron oxidized product compared to that of neutral 2. It is therefore concluded that at low temperatures the one-electron oxidized product [Ru{RuCp(CO)$_2$}$_2$(CO)$_2$(iPr-DAB)]$^{+*}$ is stable both on the voltammetric and the spectroelectrochemical time scales. This is the first time that a stable radical cation has been spectroscopically characterized for complexes [Ru(L$_1$)(L$_2$)(CO)$_2$(α-diimine)], albeit at low temperatures.

![Figure 4.6 IR spectral changes upon oxidation of 2 in butyronitrile at 193 K. The insets are the parent compound (A), the corresponding radical cation (B) and the secondary oxidation products [Ru(nPrCN)$_2$(CO)$_2$(iPrDAB)]$^{2+}$ and [RuCp(nPrCN)(CO)$_2$]$^{+}$, indicated by x and o, respectively (C). The asterisk denotes a small [RuCp(CO)$_2$]$_2$ impurity in the starting compound.](image)

The second anodic step of 2 (O2) became separated from the reversible O1 step at 213 K, but remained completely irreversible (Figure 4.5C). The corresponding oxidation of 2$^{+*}$, followed in situ by IR-spectroscopy at 193 K produced species with $\nu$(CO) at 2116, ~2060 and 2079, 2030 cm$^{-1}$. The latter two bands are again attributable to [RuCp(nPrCN)(CO)$_2$]$^{+}$, while the former two bands must be due to a highly positively charged species, e.g.
[Ru(nPrCN)₂(CO)₂(iPr-DAB)]²⁺. The secondary oxidation products of 2²⁺ were reduced back at RR2, resulting in a mixture of the parent complex 2 and [RuCp(CO)₂]²⁺.

In THF at room temperature, the irreversible reduction of 1 at R1 (see Table 4.4) produced the IR-detectable anions [Ru(SnPh₃)(CO)₂(iPr-DAB)]⁻ (ν(CO) at 1924 and 1855 cm⁻¹)⁵ and [RuCp(CO)₂]⁻ (ν(CO) at 1887 and 1801 cm⁻¹, close to the literature data²⁰). In addition to these main bands a smaller ν(CO) peak arose at 1782 cm⁻¹. This peak can be assigned to the dimer [RuCp(CO)₂]₂, its remaining peaks being hidden under the other ν(CO) bands (see Table 4.4). The reduction path of 1 is therefore proposed to involve initially an unstable radical anion, which rapidly falls apart into the stable [Ru(SnPh₃)(CO)₂(iPr-DAB)]⁻ anion and the [RuCp(CO)₂]⁻ radical (see Scheme 4.2). The latter species partly dimerizes, but its majority is reduced to the [RuCp(CO)₂]⁻ anion at the reduction potential of 1. The fact that the latter reduction potential is similar to that of [Ru(SnPh₃)(CO)₂(iPr-DAB)]⁺ indicates that reduction takes place primarily on the Ru(iPr-DAB) moiety.

The radical anion 1⁻ could only be detected by cyclic voltammetry in butyronitrile at sufficiently low temperatures (Figure 4.5B). At 213 K the reduction of 1 is a chemically partly reversible one-electron process with I/Iₕ = 0.78 at v = 100 mV/s (see Figure 4.4B). The final reduction products [Ru(SnPh₃)(CO)₂(iPr-DAB)]⁻ and [RuCp(CO)₂]⁻ are oxidized at similar electrode potentials (Table 4.4). Therefore, on the reverse anodic scan the oxidation of the two anions cannot be distinguished and appears as a single anodic peak (RO2) at -1.18 V (THF, room temperature) and -1.00 V vs Fc/Fc⁺ (butyronitrile, 213 K, Figure 4.5B). IR spectroelectrochemistry revealed that reoxidation of both anions at room temperature at RO2 mainly regenerates the parent complex 1. In addition a minor amount of the dimer [Ru(SnPh₃)(CO)₂(iPr-DAB)]₂ was produced at the end of the reoxidation. Obviously, [Ru(SnPh₃)(CO)₂(iPr-DAB)]⁻ was present in a small excess in the thin solution layer after the reduction and therefore, once all [RuCp(CO)₂]⁻ had been consumed in the course of the parallel reoxidation, the remaining [Ru(SnPh₃)(CO)₂(iPr-DAB)]⁻ was oxidized to give the dimer via a previously reported ECEC path.⁵

The reduction of 2 at R1 (Figure 4.5D, Table 4.4) is completely chemically irreversible at moderate voltammetric scan rates, independent of temperatures between 293 and 193 K. Corresponding IR spectroelectrochemical experiments again showed the formation of the [RuCp(CO)₂]⁻ anion (ν(CO) at 1887 and 1801 cm⁻¹). Two other ν(CO) bands observed at 1927 and 1847 cm⁻¹ are tentatively ascribed to the thermally unstable [Ru{RuCp(CO)₂}(CO)₂(iPr-DAB)]⁻ anion. Attempts to prevent its decomposition by carrying
out the reduction of 2 in butyronitrile at 193 K were not successful. Considering the combined voltammetric and spectroelectrochemical results, we conclude that the reduction of 2 initially yields the radical anion \[ [\text{Ru}\{\text{RuCp(CO)}_2\}(\text{CO})_2(\text{iPr-DAB})]^{-} \] which rapidly dissociates into \([\text{Ru}\{\text{RuCp(CO)}_2\}(\text{CO})_2(\text{iPr-DAB})]^{-} \) and \([\text{RuCp(CO)}_2]^{+} \). The latter radical further reduces to the corresponding anion. No dimerization of the latter radical was observed in this case, probably due to the more negative reduction potential of 2 (see Table 4.4). The former anion is thermally unstable and dissociates into another equivalent of \([\text{RuCp(CO)}_2]^{-} \) and unidentified carbonyl products. This decomposition also explains the fact that the reverse oxidation at the anodic peak R02 at -1.27 V (THF, room temperature) and -1.06 V vs Fe/Fe\(^+\) (butyronitrile, 213 K, Figure 4.5D) only concerns the \([\text{RuCp(CO)}_2]^{+} \) anion, yielding mainly the \([\text{RuCp(CO)}_2]_2 \) dimer instead of recovering the parent complex 2.

![Scheme 4.2 Reduction and oxidation pathways of 1 in nPrCN.](image)

The redox behaviour of the complexes 1 (Scheme 4.2) and 2 (Scheme 4.3) differs considerably from that of the complexes \([\text{Ru}(L_1)(L_2)(\text{CO})_2(\text{iPr-DAB})] (L_1, L_2 = \text{GePh}_3, \text{SnPh}_3, \text{PbPh}_3; \text{not all combinations were investigated}) \) previously studied in our laboratory. The latter complexes are reduced reversibly even at room temperature, producing fairly stable radical anions. In contrast, their oxidation is completely irreversible in the temperature range available. Apparently, coordination of the SnPh\(_3\) axial ligands contributes significantly to the
Chapter 4. Excited State and Redox Properties of Complexes Bearing RuCp(CO)₂ ligands

stability of the radical anion, mainly due to the strong delocalization of the SOMO over the \((\text{Ph}_3\text{Sn})_2\text{Ru(iPr-DAB)}\) moiety and also due to the strong Ru–Sn bond.¹ On the other hand, the \([\text{RuCp(CO)}_2]\) units exert a stabilizing influence on the radical cation, where the π-donor Cp-rings compensate for the reduced electron density on the axial ruthenium atom(s), compared to the neutral precursors. This property of Cp-rings has been recognized e.g. in the complexes \([\text{RuCpX(iPr-DAB)}]\) (X = Cl, OTf, \(\eta^2\)-ethene, py).²¹

![Scheme 4.3 Reduction and oxidation pathways of 2 in nPrCN.](image)

4.5 Conclusions

The incorporation of strongly donating \([\text{RuCp(CO)}_2]\) group(s) as axial ligand(s) in \([\text{Ru(L}(1)\text{L}(2))(\text{CO})_2\text{(iPr-DAB)}]\) yields complexes with a relatively high-lying \(\sigma(\text{L}_1-\text{Ru-L}_2)\) HOMO. This is reflected in relatively negative oxidation potentials of 1 and 2 compared to other \([\text{Ru(L}(1)\text{L}(2))(\text{CO})_2\text{(iPr-DAB)}]\) complexes.¹ ² As a further consequence the emission shifts to the near infrared (NIR) spectral region, with lifetimes in the order of 10 μs at 80 K. This property is very interesting from the viewpoint of the potential use of this type of complexes as NIR emitting labels.²²⁻²⁵ However, the photochemical reactivity of the studied complexes, which involves homolytic cleavage of a Ru–Ru bond as the primary photoprocess, presents a serious obstacle for such applications. The \([\text{RuCp(CO)}_2]\) group(s) also split off upon electrochemical reduction and oxidation of the complexes. The most remarkable difference between the redox behaviour of 1 and 2 in comparison with the previously studied
Chapter 4. Excited State and Redox Properties of Complexes Bearing RuCp(CO)$_2$ ligands

[Ru(L$_1$)(L$_2$)(CO)$_2$(iPr–DAB)] complexes$^5$ is the stabilizing influence of the [RuCp(CO)$_2$] groups on the one-electron-oxidized products.

4.6 References

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20) Brookhart, M.; Studabaker, W. B.; Husk, G. R.; Organometallics 1987, 6, 1141.
CHAPTER 5

FT-EPR Study of Methyl Radicals Photogenerated from
[Ru(Me)(SnPh₃)(CO)₂(iPr–DAB)] and [Pt(Me)₄(iPr–DAB)]:
An Example of a Strong Excitation Wavelength Dependent
CIDEP Effect

Van Slageren, J.; Martino, D.M.; Kleverlaan, C.J.; Bussandri, A.P.; van Willigen, H.;
Chapter 5. Photochemical Methyl Radical Formation Studied by FT-EPR

5.1 Abstract

The photoinduced methyl radical formation from the title complexes \([\text{Ru}(\text{R})(\text{SnPh}_3)(\text{CO})_2(\text{iPr}-\text{DAB})]\) \((\text{R} = \text{CH}_3, \text{CD}_3; \text{iPr}-\text{DAB} = N,N'\text{-diisopropyl-1,4-diaza-1,3-butadiene})\) and \([\text{Pt}(\text{Me})_4(\text{iPr}-\text{DAB})]\) was the subject of a detailed time resolved Fourier transform EPR (FT-EPR) study. The FT-EPR spectra of the radicals show pronounced Chemically Induced Dynamic Electron Polarization (CIDEP) effects due to the \(S_{0}\) and \(S_{1}\) radical pair mechanisms (RPM). The relative contributions of the two CIDEP mechanisms depend on solvent polarity and viscosity. In the case of the \([\text{Ru}(\text{R})(\text{SnPh}_3)(\text{CO})_2(\text{iPr}-\text{DAB})]\) complexes, the polarization pattern is also strongly excitation wavelength dependent. This effect is attributed to extremely fast reactions from different thermally non-equilibrated Sigma-Bond-to-Ligand Charge Transfer (SBLCT) excited states.

5.2 Introduction

Many studies have been made of the photochemical alkyl radical formation from transition metal\(^1\)\(^{-10}\) and main group metal\(^11\)\(^{-13}\) compounds with alkyl ligands. Alkyl radicals can be used as addition polymerization initiators\(^14\) or reagents in organic synthesis.\(^15\) Therefore, these types of metal–alkyl compounds can be very useful in these fields.\(^16\)

Detailed (time-resolved) spectroscopic studies revealed that in the case of the complexes \([\text{Re}(\text{R})(\text{CO})_3(\text{dmb})]\) \((\text{R} = \text{Me, Et, iPr; dmb} = 4,4'\text{-dimethyl-2,2'-bipyridine})\)\(^2\)\(^{-4}\) and \([\text{Ru}(\text{I})(\text{R'})(\text{CO})_2(\text{iPr}-\text{DAB})]\)\(^5\)\(^{-17}\) \((\text{R'} = \text{iPr, Bz; iPr}-\text{DAB} = N,N'\text{-diisopropyl-1,4-diaza-1,3-butadiene})\) radical formation proceeds through a metal–alkyl bond homolysis reaction from a Sigma-Bond-to-Ligand Charge Transfer (SBLCT) state. This reactive excited state is populated from an optically excited state that has predominant Metal-to-Ligand Charge Transfer (MLCT) character. In the case of \([\text{Ru}(\text{L}_1)(\text{L}_2)(\text{CO})_2(\text{iPr}-\text{DAB})]\) \((\text{L}_1, \text{L}_2 = \text{alkyl group or metal fragment})\) and \([\text{Pt}(\text{Me})_4(\text{iPr}-\text{DAB})]\), the lowest energy transition has SBLCT character. In these complexes, the SBLCT state is fairly stable and long-lived in the case of e.g. \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{iPr}-\text{DAB})]\)\(^18\) but very reactive for e.g. \([\text{Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(\text{iPr}-\text{DAB})]\) \((1\text{H})\) and \([\text{Pt}(\text{Me})_4(\text{iPr}-\text{DAB})]\) \((2)\)\(^1\)\(^{,6}\)

Our recent work has shown that Fourier transform EPR (FT-EPR) spectroscopy can be a very useful technique in studies of the mechanism of photoinduced radical formation from
organometallic complexes. Analysis of the Chemically Induced Dynamic Electron Polarization (CIDEP) effects, which are caused by spin-selective photophysical and photochemical processes, gave insight into the dynamics of alkyl radical formation. FT-EPR studies showed that the radical formation occurs from a precursor with triplet character in these cases. Apart from our own studies, one other time-resolved EPR study in organometallic chemistry is known.

In spite of our successful application of the FT-EPR technique in the field of organometallic photochemistry, the remarkably strong dependence of CIDEP effects on the nature of ligands and solvent found in our earlier work were not fully understood. Here we present a detailed FT-EPR study of the (deuterated) methyl radical formation from the organometallic complexes [Ru(R)(SnPh)(CO)(iPr-DAB)] (R = CH₃, CD₃) (1H and 1D respectively) and [Pt(Me)(iPr-DAB)] (2). Of particular interest is the finding that the methyl radical spectra in the case of 1 display a spin polarization pattern that is strongly dependent on excitation wavelength. A preliminary account of this work has appeared in the literature.

5.3 Experimental Section

The complexes [Ru(R)(SnPh)(CO)(iPr-DAB)] (R = CH₃, CD₃; iPr-DAB = N,N'-diisopropyl-1,4-diaza-butadiene) (1H and 1D respectively), and [Pt(Me)(iPr-DAB)] (2) were synthesized according to literature procedures. Toluene, dichloromethane, methanol, 2-propanol, ethylene glycol and 1,2-propane diol (Aldrich) were used as received.

FT-EPR measurements were performed with a home-built spectrometer. The response of the sample to the π/2 microwave pulses was detected in quadrature with application of the CYCLOPS phase cycling routine. All measurements were performed at room temperature. Solutions of the complexes (ca. 1–2 mM) were freed of oxygen by purging with argon prior to and during measurements. The solutions were pumped through a quartz EPR flow cell held in the microwave cavity. The second or third harmonic of a Quanta Ray GCR12 Nd:YAG laser (~20 mJ/pulse, 10 Hz) was used for excitation at 532 or 355 nm, a Lambda-Physik EMG103 MSC XeCl excimer laser for excitation at 308 nm (~20 mJ, 10 Hz), and an excimer laser pumped dye laser (Lambda-Physik FL 3001, ~2 mJ, 10 Hz) for excitation at 440 nm. Unless noted otherwise, 400 FIDs (100 per phase) were averaged to obtain the spectra.

The time evolution of transient spectra was measured as follows. The FID produced by a π/2 (15 ns) microwave pulse was recorded for a series of delay times τ₀ (10 ns to 5 μs) between laser and
microwave pulses. Amplitudes, linewidths, and phases of resonance peaks were derived from the FIDs with a LPSVD analysis routine.\textsuperscript{26} Since the spectra of the methyl radicals cover a frequency range that far exceeds the bandwidth of the spectrometer, EPR spectra presented in the figures are assembled from FIDs obtained with a set of distinct field values. Spectra from the deuterated methyl radical were obtained at a single field setting. Spectral intensities were corrected for photochemical decomposition during the measurement. Corrections for the variation in signal intensity with change in frequency offset were based on calibration data given by a free radical reference.

\begin{figure}[h]
\begin{center}
\includegraphics[width=\textwidth]{image.png}
\end{center}
\caption{Schematic molecular structures and electronic absorption spectra of [Ru(Me)(SnPh\textsubscript{3})(CO)\textsubscript{2}(iPr-DAB)] (1H) and [Pt(Me)\textsubscript{4}(iPr-DAB)] (2) in toluene.}
\end{figure}

### 5.4 Results

Figure 5.1 shows the complexes under study as well as their electronic absorption spectra. The lowest-energy absorption band of the title complexes lies between 500 and 550 nm. The band was attributed to the $\sigma \rightarrow \pi^*$ or Sigma-Bond-to-Ligand Charge Transfer (SBLCT) transition from the HOMO (which has $\sigma$(Sn-Ru-Me) or $\sigma$(Me-Pt-Me) character, respectively) to the $\pi^*$(iPr-DAB) LUMO.$^{1,18}$

The FT-EPR spectra of the radicals produced by irradiation of 1H and 1D in toluene for delay times of 50 ns and 1 $\mu$s are shown in Figure 5.2. The spectra are assigned to the
Chapter 5. Photochemical Methyl Radical Formation Studied by FT-EPR

CH$_3^\cdot$ and CD$_3^\cdot$ radicals on the basis of measured hyperfine splitting constants (hfsc) of 2.27 mT (CH$_3^\cdot$) and 0.33 mT (CD$_3^\cdot$) which are in close agreement with literature values.\(^{27,28}\) It is noted that the FT-EPR spectra do not show a signal contribution due to the [Ru(SnPh$_3$)(CO)$_2$(iPr–DAB)]$^{\cdot}$ or [Pt(Me)$_3$(iPr–DAB)]$^{\cdot}$ radicals, probably due to their short $T_2$ values. This prevents detection of FT-EPR spectra because of the instrument dead time. The $g$ values of the [M(CO)$_3$(tBu–DAB)]$^{\cdot}$ (M = Mn, Re) radicals were found at values (2.0043 and 2.0059 respectively)\(^{29}\) similar to that of the radical anion of the free ligand (2.0034).\(^{30}\) The $g$ values of [Ru(SnPh$_3$)(CO)$_2$(iPr–DAB)]$^{\cdot}$ or [Pt(Me)$_3$(iPr–DAB)]$^{\cdot}$ radicals are probably similar to those of [M(CO)$_3$(tBu–DAB)]$^{\cdot}$ (M = Mn, Re), because all these complexes are structurally and electronically very similar. This means that the $g$ values of the [Ru(SnPh$_3$)(CO)$_2$(iPr–DAB)]$^{\cdot}$ or [Pt(Me)$_3$(iPr–DAB)]$^{\cdot}$ radicals are close to those of the CH$_3^\cdot$ and CD$_3^\cdot$ radicals (2.00255). Since for the metal centered [Mn(CO)$_3$(PBu$_3$)$_2$]$^{\cdot}$ radical a higher value of 2.030 was found,\(^{31}\) it was concluded that the odd electron in [M(CO)$_3$(tBu–DAB)]$^{\cdot}$ (M = Mn, Re) is mainly localized on the tBu–DAB ligand.

![Figure 5.2. FT-EPR spectra of the methyl radicals produced by photoexcitation (532 nm) of ~1 mM [Ru(R)(SnPh$_3$)(CO)$_2$(iPr–DAB)], R = CH$_3$ (1H, left) or CD$_3$ (1D, right) in toluene for short (50 ns) and long (1 μs) delay times. Note that the field range of the CD$_3^\cdot$ spectra is smaller than that of the CH$_3^\cdot$ spectra and that absorption peaks point up.](image)

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Chapter 5. Photochemical Methyl Radical Formation Studied by FT-EPR

The CH$_3^*$ and CD$_3^*$ spectra obtained with $\tau_d = 50$ ns show a low-field-emission/ high-field-absorption (E/A) CIDE P pattern. In the case of the former radical an additional net emission component is observed ($E^\text{v}/A$), while in the latter a net absorption contribution is present ($E/A^*$). It is clear that the CH$_3^*$ radical spectrum (Fig. 5.2A) has a much larger signal-to-noise ratio than that of the CD$_3^*$ radical (Fig. 5.2B). Since the photoreactivities of 1H and 1D are the same and the spectra were recorded using solutions with similar concentrations, this indicates that the electron polarization generated in the formation of CH$_3^*$ is much larger than that of CD$_3^*$.

**Figure 5.3** FT-EPR spectra of the methyl radicals produced by photoexcitation (532 nm) of ~1 mM solutions of 1H (left) and 2 (right) in (from top to bottom) toluene, dichloromethane, and methanol at 50 ns delay time. Solvent viscosities, $\eta$ (in mPa.s), and relative dielectric constants $\varepsilon_r$ are included.

As shown in Figure 5.2 (C, D), at $\tau_d = 1$ $\mu$s the spin systems are close to thermal equilibrium. An analysis of the time profiles (not shown) of the intensities of the resonance peaks of the CH$_3^*$ radical in toluene at room temperature shows an exponential decay to thermal equilibrium with a rate constant of $9.5(0.8) \times 10^6$ s$^{-1}$ corresponding to a spin–lattice relaxation time of 105(13) ns. By comparison, a $T_1$ measurement of the methyl radical
generated by pulse radiolysis in aqueous solution gave a value of 0.2 μs.\textsuperscript{32} For the CD\textsubscript{3}\textsuperscript{*} radical a value of 74(40) ns is found. The large uncertainty in this value is due to the relatively poor signal-to-noise which reflects the absence of strong signal enhancement by CIDEP.

![FT-EPR spectra](image)

Figure 5.4. FT-EPR spectra of the methyl radicals produced by photoexcitation (532 nm) of ~1 mM 1H (left) and 2 (right) in (from top to bottom) methanol, 2-propanol, ethylene glycol, and 1,2-propane diol at 50 ns delay time. Solvent viscosities, η (in mPa.s), and relative dielectric constants ε\textsubscript{r} are included.

To determine the operative CIDEP mechanisms unambiguously, the solvent effect on the polarization pattern observed in the spectra of the CH\textsubscript{3}\textsuperscript{*} radicals, obtained by irradiation of solutions of 1H and 2, was investigated. First the solvent polarity was varied, keeping the viscosity at a similar value. The results are shown in Figure 5.3, together with the viscosities η (in mPa.s) and relative dielectric constants ε\textsubscript{r} of the solvents (the latter values are used as
indication of solvent polarity). It can be seen that going from toluene to dichloromethane and finally to methanol, i.e. with increasing solvent polarity, the net emission signal contribution to the spectra increases relative to the E/A contribution. When taking into account the dielectric loss due to the solvent on signal intensity, the signal-to-noise ratios of all the spectra are fairly similar.

Figure 5.5. Laser excitation wavelength dependence of the FT-EPR spectra of the methyl radical produced by photoexcitation of 1H (left) and 1D (right) dissolved in toluene for a delay time of 50 ns. With 440 nm excitation, signals are the average produced by 4000 laser shots.

In contrast, the signal intensity clearly increases upon increasing the solvent viscosity in the case of 2 (Figure 5.4). The decrease in signal intensity per measurement stays constant, indicating a similar photochemical quantum yield in all solvents. In the case of 1H a complication arises due to the limited solubility of the complex when using ethylene glycol or
1,2-propanediol as solvents. In both systems the length of the free-induction decay (FID) increases, which transforms to narrower lines in the frequency domain. From the increase in signal intensity, it is clear that an increase in solvent viscosity leads to a pronounced increase in a signal contribution stemming from a particular CIDEP mechanism, rather than a decrease of another component. It should be noted that the hyperfine dependent polarization pattern remains unaffected by the strong increase in solvent viscosity, proving that the increased polarization is due to a hyperfine dependent CIDEP mechanism. No strong solvent dependence of the polarization pattern was observed for 1D, the importance of which will be discussed hereafter.

Finally, the influence of the excitation wavelength on the polarization pattern was investigated by recording FT-EPR spectra for 1H, 1D and 2, using 308, 355, 440 and 532 nm irradiation. The surprising results for 1H and 1D in toluene are depicted in Figure 5.5. Excitation at shorter wavelengths leads to a shift in polarization pattern from $E^*/A$ to $E/A^*$ for 1H and from $E/A^*$ to $A$ for 1D. For the latter complex this shift is accompanied by a large increase in signal intensity. The polarization patterns observed for radicals generated from 1H using short wavelength irradiation seem to be less solvent sensitive than those observed using long wavelength irradiation, since the results for 1H are virtually the same in methanol and toluene (not shown). In contrast, no influence of the excitation wavelength on the polarization pattern was observed in the case of 2. In a recent study on the photoinduced reactions of xanthone with alcohols, a slight excitation wavelength dependence of the polarization pattern was observed.\textsuperscript{33,34} An earlier example\textsuperscript{35} was later disputed.\textsuperscript{36}

### 5.5 Discussion

All the recorded FT-EPR spectra in this study display an $E/A$ pattern to some extent. This is a clear indication that the $S_{T0}$ radical pair mechanism (RPM) is operative and that the radicals are formed from a triplet excited state precursor (assuming the sign of the exchange interaction is negative, \textit{i.e.} the singlet radical pair state is lower in energy than the triplet).\textsuperscript{37} In its usual form, this mechanism is a three-step process. After formation of the geminate radical pair, the radicals diffuse apart which decreases the exchange interaction, allowing the singlet level and the $T_{0}$ component of the triplet level to mix through the hyperfine coupling. The magnitude of the polarization created in this way is a function of the difference in resonance
Chapter 5. Photochemical Methyl Radical Formation Studied by FT-EPR

frequencies between the two (hyperfine components of the) radicals that form the radical pair.\textsuperscript{37,38} The finding that deuteration strongly decreases the polarization magnitude (cf. Fig. 5.2A and 5.2B) establishes that the difference in resonance frequencies must be primarily determined by the hyperfine coupling constant. A comparison of the signal intensities of the spectra from 1D at short and long delay times (cf. Fig. 5.2) shows that the CIDEP and Boltzmann signals are of similar magnitude. Given the short $T_1$, this means that the observed intensity pattern in the spectrum for 1D (Fig. 5.2B) can be satisfactorily explained by a combination of Boltzmann and ST\textsubscript{0} RPM signal contributions.

As shown in Figure 5.3, an increase in solvent polarity leads to a decrease in polarization due to the ST\textsubscript{0} RPM in the spectra of 1H and 2 (cf. Fig. 5.3). Apparently, the more polar solvents can cause the radical pair to break up at some point before the final reencounter step of the ST\textsubscript{0} RPM. Upon increase of the solvent viscosity, in polar solvents where the ST\textsubscript{0} RPM signal contribution is small, the net emissive signal contribution is strongly enhanced for 1H and 2 (cf. Fig. 5.4), but not for 1D. This suggests that this contribution is due to a CIDEP mechanism in which the polarization is generated by hyperfine interaction as well. The contribution is attributed to the ST\textsubscript{-1} RPM \textsuperscript{37,39,40} in which the singlet level interacts with the T\textsubscript{-1} component of the triplet level, rather than with the T\textsubscript{0} component. This one step mechanism is generally only operative in cases of high solvent viscosity and/or large hyperfine interaction. This mechanism generates a net emissive spectrum with stronger polarization in the low field than in the high field part of the spectrum. Exactly this pattern is observed when employing a very high viscosity solvent (Figure 5.4). The operation of this mechanism in a polar solvent suggests also that the ST\textsubscript{0} RPM contribution is diminished due to prevention of the reencounter step rather than more rapid break up of the geminate radical pair.

The triplet mechanism (TM) which is often invoked to explain net polarization patterns could in principle also give rise to the observed net emission contribution in the spectra of 1H and 2. In this mechanism, spin polarization is created through spin-selective intersystem crossing (ISC) from the singlet to the triplet excited state.\textsuperscript{37,41} This polarization is then transferred to the radicals. The magnitude of the hyperfine independent TM polarization depends on solvent viscosity and reaction rate.\textsuperscript{41,42} An increase in viscosity increases the rotational correlation time leading to a larger spin polarization. Apart from the hyperfine dependence of the polarization pattern, this matches our experimental observations. For TM CIDEP to make a significant signal contribution, the reaction rate ($k_t$) should be large enough to compete with the rate of spin–lattice relaxation of the triplet which typically is $\geq 10^9$ \textit{s}^{-1}. 104
On the other hand, if the reaction rate is fast compared to the electron spin Larmor frequency, $k_t > \omega_0$, spin-selective ISC does not give rise to TM CIDEP. There are indications that the photochemical reaction rate is indeed very high. Firstly, the observed photochemical quantum yield of ca. 0.5 is temperature independent and excitation wavelength dependent throughout the lowest-energy absorption band. This suggests that the photochemical reaction is an activationless process in competition with vibrational relaxation. Secondly, for a related complex, $[\text{Re(Me)(CO)}_3(\text{dmb})]$ ($\text{dmb} = 4,4'$-dimethyl-2,2'-bipyridine), the excited state lifetime was experimentally determined to be shorter than 400 fs. Several other examples of ultrafast photochemical reactions in organometallic chemistry have been reported in the literature. A final argument against a TM contribution, is the fact that the solvent viscosity has no influence on the polarization pattern in the case of 1D. This would be expected if the hyperfine independent TM were operative (vide supra).

The excitation wavelength dependence of the polarization pattern found for 1H and 1D (cf. Fig. 5.5) can also be explained by the fact that optical excitation is followed by a reaction from thermally non-equilibrated excited states (a so-called prompt chemical reaction). As noted before, the lowest-energy absorption band of 1 and related complexes has been assigned to a $\sigma(\text{Sn-Ru-Me}) \rightarrow \pi^*(\text{iPr-DAB})$ (SBLCT) transition on the basis of the resonance Raman and time-resolved IR spectra, and DFT MO calculations on model complexes such as $[\text{Ru(SnH}_3)(\text{Me})(\text{CO})_2(\text{H-DAB})]$. According to these calculations the $\sigma(\text{Sn-Ru-Me})$ HOMO is a delocalized orbital, which consists of contributions from $p_x$(Ru), the antisymmetric sp$^3$(Sn)-sp$^3$(Me) combination and $\pi^*(\text{H-DAB})$. Similarly, the first electronic transition of 2 is the $\sigma(\text{Me-Pt-Me}) \rightarrow \pi^*(\text{iPr-DAB})$ (SBLCT) transition. The second electronic transition of complexes 1 and 2 found at 388 nm for 1H and at 326 nm for 2 (in toluene cf. Fig. 5.1) belongs to a d$_\delta$(Ru, Pt) $\rightarrow \pi^*(\text{iPr-DAB})$ (MLCT) transition. In contrast to the SBLCT state, this MLCT state is not reactive and MLCT excitation will only result in radical formation via occupation of the lower lying reactive SBLCT state. In agreement with this, irradiation of 2 into its second absorption band with 355 nm results in exactly the same polarization pattern as found upon 532 nm excitation.

In the case of 1H, 440 and 532 nm excitation give again rise to the same polarization pattern. With the available setup irradiation of 1H into its second absorption (MLCT) band at 388 nm was not possible. Surprisingly, the use of 355 nm excitation gave rise to a polarization pattern different from that observed at 440 and 532 nm, but exactly as that found upon 308 nm irradiation. Apparently, the radicals formed on 355 nm excitation are not produced from
the lowest SBLCT state via MLCT excitation as for 2. In view of the close similarity of the polarization patterns, the radicals obtained by 355 and 308 nm excitation are most likely both produced from a thermally non-equilibrated excited state at higher energy.

A likely candidate for this higher lying excited state is the second SBLCT state. According to DFT MO calculations, the model complex [Ru(SnH$_3$)$_2$(CO)$_2$(H–DAB)]$^{50}$ has indeed a second $\sigma$(Sn–Ru–Sn) orbital, consisting of contributions from $d_\chi$(Ru) and the symmetric sp$^3$(Sn)+sp$^3$(Sn) combination. A second SBLCT transition, i.e. $\sigma$(Sn–Ru–Sn) $\rightarrow$ $\pi^\ast$(H–DAB) will originate from this orbital and is expected ca. 2 eV higher in energy than the first SBLCT transition. The first SBLCT transition lies at 531 nm for 1 and hence the second SBLCT transition should be at about 300 nm for 1. This second SBLCT state will also be reactive and the different polarization patterns in the FT-EPR spectra of 1 are therefore attributed to the formation of radicals by prompt chemical reaction from the two different SBLCT states. In the case of 2, the energy difference between the two $\sigma$(Me–Pt–Me) orbitals is expected to be much larger (3.3 eV), according to DFT MO calculations of [Pt(Me)$_4$(iPr–DAB)].$^{51}$ This should position the second SBLCT transition at about 220 nm, which explains the absence of any wavelength effect for 2.

The above explanation is supported by the absence of any wavelength dependence of the CIDEP pattern in the case of the related complexes [Ru(I)(iPr)(CO)$_2$(iPr–DAB)] and [Re(R)(CO)$_3$(4,4'-dimethyl-2,2'-bipyridine)] (R= Et, iPr).$^3$ These complexes only have a single $\sigma$(M–R) bond and therefore only one low-lying SBLCT state from which radicals are formed.

For both 1H and 1D a strong increase in absorptive contribution to the CIDEP pattern is observed on short wavelength irradiation, suggesting that this additional component is due to a hyperfine independent mechanism. Apart from the TM, one other hyperfine independent mechanism is known: the spin–orbit coupling induced polarization mechanism (SOCM).$^{52,53}$ This mechanism involves spin-selective back reaction from a triplet contact radical pair to the singlet ground state, which leads to selective depopulation of certain triplet sublevels. However, since this mechanism is independent of the excitation wavelength, it is unlikely to be operative.
5.6 Conclusions

Numerous studies dealing with spin selectivity of photochemical reactions involving transition metal complexes have been published in recent years.54,55 Most of these papers deal with magnetic field effects on reaction dynamics and very few are concerned with applications of time-resolved EPR. The results presented here and in previous work 2,19,20 show that investigations with time-resolved EPR techniques can contribute to the understanding of the mechanisms of photochemical reactions involving transition metal complexes.

5.7 References


Chapter 5. Photochemical Methyl Radical Formation Studied by FT-EPR

Chapter 5. Photochemical Methyl Radical Formation Studied by FT-EPR
The Complexes cis-[Rh(R)₂(I)(CO)(dmb)] (R = Me, iPr; dmb = 4,4'-dimethyl-2,2'-bipyridine): Synthesis, Structure and Photoreactivity

Chapter 6. The complexes cis-[Rh(R)_{2}(I)(CO)(dmb)]: Synthesis, Structure and Photoreactivity

6.1 Abstract

In this chapter the synthesis, structure and photochemistry of the novel rhodium(III) complexes cis-[Rh(R)_{2}(I)(CO)(dmb)] (R = Me (1), iPr (2)) are described. Although many di- and trimethyl-rhodium(III) complexes are known, cis-[Rh(iPr)_{2}(I)(CO)(dmb)] (2) is the first diisopropyl-rhodium(III)) compound. Single crystal X-Ray diffraction studies revealed the structure of 1. The lowest electronic transition has Halide-to-Ligand Charge Transfer character according to resonance Raman spectra, obtained by excitation into the corresponding absorption band. Upon irradiation in solution, both 1 and 2 give rise to Rh–R bond homolysis as evidenced by spin-trap EPR investigations. The photoreaction occurs after crossing to the reactive Sigma-Bond-to-Ligand Charge Transfer (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.

6.2 Introduction

Complexes with a lowest Metal-to-Ligand Charge Transfer (MLCT) state, such as [Ru(bpy)_{3}]^{2+} and [Re(Cl)(CO)_{3}(bpy)] have been extensively studied with regard to their excited state properties. By replacement of the chloride in the latter complex by a strongly σ donating ligand L, such as an alkyl group or metal fragment, σ(Re–L) of [Re(L)(CO)_{3}(α-diimine)] may become the HOMO. As a result, the lowest excited state obtains Sigma-Bond-to-Ligand Charge Transfer (SBLCT) character.\textsuperscript{1,2} The photochemical properties of the complexes [Re(L)(CO)_{3}(α-diimine)] have been studied extensively in our laboratory.\textsuperscript{3-5} It was found that occupation of the SBLCT excited state can give rise to efficient Re–L bond homolysis. Later these studies were extended to [M(L)_{1}(L)_{2}(CO)_{2}(α-diimine)] (M = Ru, Os) and [Pt(L)_{2}(Me)_{2}(α-diimine)].\textsuperscript{5-8} However, not many complexes are known from group 9, in which low lying SBLCT states are present. One well studied example is vitamin B12 and its model complexes,\textsuperscript{9} for which the SBLCT excited state was proposed to be responsible for the observed Co–C bond splitting.\textsuperscript{10} Apart from these examples, to our knowledge the only group 9 organometallic complexes shown to possess such SBLCT excited states are fac-[Ir(III){tris-(6-isopropyl-8-quinolyl)dioxidogenosilyl}],\textsuperscript{11,12} and [Ir(R)(CO)(PPh_{3})_{2}(mnt)] (R = Me, Et; mnt = maleonitriledithiolate).\textsuperscript{13}
Chapter 6. The complexes cis-{Rh(R)_2(I)(CO)(dmb)}: Synthesis, Structure and Photoreactivity

Here we present the synthesis, structure and photochemistry of two novel complexes [Rh(R)_2(I)(CO)(dmb)] (R = Me (1), iPr (2); dmb = 4,4'-dimethyl-2,2'-bipyridine).

6.3 Experimental Section

**Materials.** I_2 (Merck), 4,4'-dimethyl-2,2'-bipyridine (dmb, Fluka), MeMgCl (3.0 M in THF, Aldrich), iPrMgCl (2.0 M in THF, Aldrich), AgNO_3 (Aldrich, 99%) were used as received. Solvents purchased from Acros (THF, hexane, pentane, dichloromethane, acetonitrile, diethyl ether, methanol, 2-MeTHF) were dried on and distilled from the appropriate drying agent when necessary. Silica gel (kieselgel 60, Merck, 70–230 mesh) for column chromatography was dried and activated by heating *in vacuo* at 160 °C overnight.

**Syntheses.** All syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. [Rh(Cl)(CO)_2]_2^14 was prepared according to a literature procedure.

[Rh(Cl)(CO)(dmb)]. To a solution of [Rh(Cl)(CO)_2]_2 in THF, 1.1 eq dmb in THF was added at -78 °C. The reaction mixture was allowed to warm to room temperature while stirring. Evaporation of the solvent and washing with hexane afforded the red product as a solid in ca. 90% yield. IR (THF); ν(CO) : 1970 cm⁻¹. UV (THF); λ_max: 501 nm. $^1$H NMR (CDCl₃); δ: 2.42 (s, 6H, dmb CH₃), 2.54, (s, 6H, dmb CH₃), 7.04 (d, $^3$J = 5.6 Hz, 2H, dmb H5), 7.29 (d, $^3$J = 5.9 Hz, 2H, dmb H5), 7.76 (s, 1H, dmb H3), 7.80 (s, 1H, dmb H3), 8.51 (d, $^3$J = 5.6 Hz, 2H, dmb H6), 9.16 (d, $^3$J = 5.8 Hz, 2H, dmb H6) ppm.

[Rh(NO_3)(CO)(dmb)]. A suspension of exactly one equivalent of AgNO_3 in a solution of 150 mg [Rh(Cl)(CO)(dmb)] in THF was stirred overnight at room temperature. Filtration and evaporation of the solvent gave the red product in near quantitative yield. IR (THF); ν(CO) : 1970 cm⁻¹. $^1$H NMR (CDCl₃); δ: 2.42 (6H, dmb CH₃), 2.54, (6H, dmb CH₃), 7.04 (2H, dmb H5), 7.29 (2H, dmb H5), 7.76 (1H, dmb H3), 7.80 (1H, dmb H3), 8.51 (2H, dmb H6), 9.16 (2H, dmb H6) ppm.

[Rh(I)_2(NO_3)(CO)(dmb)]. Dropwise addition of one equivalent of I_2 in THF to a solution of 100 mg [Rh(NO_3)(CO)(dmb)] in THF at -78 °C, overnight stirring at room temperature and subsequent evaporation of the solvent yielded the crude product. Washing with pentane gave the pure orange-brown product in ca. 80% yield. IR (THF); ν(CO) : 2098 cm⁻¹. $^1$H NMR (CDCl₃); δ: 2.64 (s, 6H, dmb CH₃), 2.68 (s, 6H, dmb CH₃), 3.75 (d, $^3$J = 5.8 Hz, 2H, dmb H5), 7.58 (d, $^3$J = 6.3 Hz, 2H, dmb H5), 7.99 (s, 2H, dmb H3), 8.66 (d, $^3$J = 6.0 Hz, 2H, dmb H6), 9.69 (d, $^3$J = 5.9 Hz, 2H, dmb H6) ppm.

cis-[Rh(Me)_2(I)(CO)(dmb)] (1). To a solution of [Rh(I)_2(NO_3)(CO)(dmb)] (100 mg) in THF at -78 °C, two equivalents of MeMgCl (3.0 M in THF) were gradually added through a syringe, while following the reaction by IR. The colour of the reaction mixture changed from brown to brown-red.

during the addition. The solid obtained after quenching of the excess of Grignard and evaporation of the solvent in vacuo, was dissolved in CH$_2$Cl$_2$ and washed repeatedly with water. Drying on anhydrous MgSO$_4$ and evaporation of the solvent yielded the crude product which was purified by column chromatography (activated silica, CH$_2$Cl$_2$/hexane gradient elution) and obtained as a yellow-brown solid in ca. 50 % yield. FAB-MS; $m/z$: [M$^+$] not detected, 817 [2M$^+$ – I] (resulting from gas phase clustering), 787 [2M$^+$ – 1 – 2 Me], 457 [M$^+$ – Me], 345 [M$^+$ – I], 315 [M$^+$ – 2 Me – I], 287 [M$^+$ – 2 Me – I – CO]. IR (THF); v(CO) : 2031 cm$^{-1}$. UV (THF); $\lambda_{\text{max}}$: 295, 370 nm. $^1$H NMR (CD$_2$Cl$_2$); $\delta$: 0.54 (d, $J_{\text{Rh-H}}$ = 2.2 Hz, 3H, Rh-Me$_{\text{ax}}$, assignment corresponding to 15). 1.18 (d, $J_{\text{Rh-H}}$ = 2.0 Hz, 3H, Rh-Me$_{\text{eq}}$), 2.53, (s, 3H, dmb CH$_3$), 7.33 (d, $J = 5.6$ Hz, 2H, dmb H5), 7.42 (d, $J = 5.3$ Hz, 2H, dmb H5), 8.07 (s, 2H, dmb H3), 8.76 (d, $J = 5.6$ Hz, 2H, dmb H6), 8.77 (d, $J = 5.3$ Hz, 2H, dmb H6) ppm. $^{13}$C NMR APT (CD$_2$Cl$_2$); $\delta$: 0.9 (d, $J_{\text{Rh-C}}$ = 22 Hz, Rh-Me$_{\text{ax}}$), 6.6 (d, $J_{\text{Rh-C}}$ = 22 Hz, Rh-Me$_{\text{eq}}$), 21.4 (dmb Me), 123.7 (dmb C3), 123.9 (dmb C3), 127.3 (dmb C5), 127.7 (dmb C5), 147.7 (dmb C6), 151.4 (dmb C6), 150.6 (dmb C4), 151.5 (dmb C4), 152.7 (dmb C2), 155.2 (dmb C2), 191.3 (J$_{\text{Rh-C}}$ = 68 Hz, CO) ppm.

cis-[Rh(iPr)$_2$]([CO](dmb)) (2). This complex was synthesized by reaction of [Rh(I)$_2$(NO$_3$)(CO)(dmb)] (100 mg) and two equivalents of iPrMgCl in Et$_2$O using the same method as for [Rh(Me)$_2$(NO$_3$)(CO)(dmb)]. The reaction product was purified by pentane extraction of the solid obtained after quenching and evaporation of the solvent. The orange-brown product was obtained in 80% yield. FAB-MS; $m/z$: [M$^+$] not detected, 929 [2M$^+$ – I] (resulting from gas phase clustering), 843 [2M$^+$ – 1 – 2 iPr], 729 [2M$^+$ – I – 4 iPr – CO], 701 [2M$^+$ – 1 – 4 iPr – 2 CO], 401 [M$^+$ – I], 315 [M$^+$ – 2 Me – I], 287 [M$^+$ – 2 Me – I – CO]. IR (THF); v(CO) : 2021 cm$^{-1}$. UV (THF); $\lambda_{\text{max}}$: 295, 370 nm. $^1$H NMR (CD$_2$Cl$_2$); $\delta$: 0.72 (ps, $J = J_{\text{Rh-H}}$ = 6.3 Hz, 3M, Rh–CH(CH$_3$)$_2$), 0.92 (m, 1H, Rh–CH(CH$_3$)$_2$ (ax, assignment corresponding to 15)), 1.09 (ps, $J = J_{\text{Rh-H}}$ = 6.3 Hz, 3H, Rh–CH(CH$_3$)$_2$), 1.24 (m, 3H, Rh–CH(CH$_3$)$_2$), 1.7 (m, 3H, Rh–CH(CH$_3$)$_2$), 2.09 (m, 1H, Rh–CH(CH$_3$)$_2$ (eq)), 2.52 (s, 3H, dmb CH$_3$), 2.58 (s, 3H, dmb CH$_3$), 7.36 (d, $J = 5.4$ Hz, 1H, dmb H5), 7.43 (d, $J = 5.1$ Hz, 1H, dmb H5), 8.02 (s, 2H, dmb H3), 8.61 (d, $J = 6.0$ Hz, 2H, dmb H6), 8.76 (d, $J = 5.4$ Hz, 2H, dmb H6) ppm. $^{13}$C NMR APT (CD$_2$Cl$_2$); $\delta$: 16.9 (d, $J_{\text{Rh-C}}$ = 2.8 Hz, Rh–CH(CH$_3$)$_2$), 18.8 (d, $J_{\text{Rh-C}}$ = 2.6 Hz, Rh–CH(CH$_3$)$_2$), 21.5 (dmb Me), 27.3 (Rh–CH(CH$_3$)$_2$), 30.4 (Rh–CH(CH$_3$)$_2$), 31.7 ($J_{\text{Rh-C}}$ = 22 Hz, Rh–CH(CH$_3$)$_2$), 33.7 ($J_{\text{Rh-C}}$ = 23 Hz, Rh–CH(CH$_3$)$_2$), 123.6 (dmb C3), 123.9 (dmb C3), 127.2 (dmb C5), 127.5 (dmb C5), 147.2 (dmb C6), 150.4 (dmb C4), 151.0 (dmb C6), 151.5 (dmb C4), 152.6 (dmb C2), 155.5 (dmb C2), 193.1 ($J_{\text{Rh-C}}$ = 73 Hz, CO) ppm.

Measurements. FAB$^+$-MS spectra were obtained on a JEOL JMS SX/SX102A four-sector mass spectrometer coupled to a JEOL MS-MP7000 data system. Infrared spectra were recorded on Bio-Rad FTS-7 and FTS-60A FTIR spectrophotometers (the latter equipped with a liquid-nitrogen-cooled MCT detector), and electronic absorption spectra on Varian Cary 4E and Hewlett-Packard 8453 spectrophotometers. NMR spectra were recorded on a Varian Mercury 300 (300.13 MHz and
75.46 MHz for $^1$H and $^{13}$C, respectively) spectrometer. Resonance Raman spectra of the complexes dispersed in KNO$_3$ pellets were recorded on a Dilor XY spectrometer equipped with a Wright Instruments CCD detector, using a Spectra Physics 2040E Ar$^+$ laser as the excitation source. EPR spectra were recorded using a Varian E-104A instrument. The radicals were generated by in situ irradiation using an Oriel high pressure mercury lamp.

**Single-crystal structure determination of 1.** Suitable crystals of 1 were grown by vapour diffusion of hexane into a solution of 1 in CH$_2$Cl$_2$ at ~20 °C. Crystal data: C$_{15}$H$_{18}$N$_2$ORh·CH$_2$Cl$_2$, FW = 557.05, colourless block, 0.36 × 0.27 × 0.12 mm$^3$, monoclinic, $P2_1/c$ (No. 14), $a = 11.0746(3)$ Å, $b = 14.1766(4)$ Å, $c = 14.5336(4)$ Å, $\beta = 119.462(2)^\circ$, $V = 1986.70(10)$ Å$^3$, $Z = 4$, $\rho = 1.862$ g cm$^{-1}$.

Intensities were measured on a Nonius KappaCCD diffractometer, with rotating anode (Mo-K$_{\alpha}$, $\lambda = 0.71073\AA$) at 150 K. The absorption correction was based on multiple measured reflections (PLATON$^{16}$, $\mu = 2.69$ mm$^{-1}$, 0.63-0.71 transmission). 17229 measured reflections, 4538 unique reflections ($R_{int} = 0.0553$). The structure was solved with direct methods (SIR-97$^{17}$) and refined with the program SHELXL-97$^{18}$ against $F^2$ of all reflections up to a resolution of $(\sin \theta/\lambda)_{max} = 0.65$ Å$^{-1}$. The two equatorial ligand positions are partially occupied by methyl and carbonyl groups, respectively. The carbon atoms were not split and refined with an occupancy of 1. For the carbonyl oxygen and the methyl hydrogens the occupancy was refined under the assumption that the total occupancy is 1. The refinement resulted in a disorder ratio of 0.677(7):0.323(7). Non hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. 221 parameters. The drawing, calculations and checking for higher symmetry were performed with the PLATON$^{16}$ package. $R(I>2\sigma(I))$: $R_1 = 0.0275$, $wR2 = 0.0635$. $R$ (all data): $R_1 = 0.0332$, $wR2 = 0.0654$. $S = 1.102$.

Crystallographic data (excluding structure factors) for the structure in this chapter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 150426. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

### 6.4 Results and Discussion

#### 6.4.1 Syntheses

The synthesis of [Rh(Cl)(CO)(\(\alpha\)-diimine)] from [Rh(Cl)(CO)$_2$I] was shown to proceed by \(\alpha\)-diimine coordination resulting in [Rh(Cl)(CO)$_2$(\(\alpha\)-diimine)], prior to CO loss.$^{19}$ This pentacoordinated complex may dissociate into an [Rh(CO)$_2$(\(\alpha\)-diimine)]$^+$[Cl]$^-$ ion pair.$^{20}$
These intermediates were isolated in several cases.\textsuperscript{21-23} The synthesis of [Rh(Cl)(CO)(dmb)] (dmb = 4,4’-dimethyl-2,2’-bipyridine) did not yield such species. Thus, the product obtained was red in accordance with the observed colour for [Rh(Cl)(CO)(bpy)],\textsuperscript{24} whereas \textit{e.g.} [Rh(CO)\textsubscript{2}(phen)]\textsuperscript{+}(ClO\textsubscript{4})\textsuperscript{-} was reported to be green.\textsuperscript{22} Moreover, only one band due to $\nu$(CO) was found in the IR spectrum at 1970 cm\textsuperscript{-1} in THF, in correspondence with literature data for [Rh(Cl)(CO)(bpy)] (1977 cm\textsuperscript{-1} in MeCN).\textsuperscript{25} In addition, $^1$H NMR showed the dmb ligand to be in an asymmetric environment, which is not the case for [Rh(CO)\textsubscript{2}(\alpha\text{-diimine})]\textsuperscript{+}(Cl\textsuperscript{-}).

Apart from these products, in the reaction of [Rh(Cl)(CO)\textsubscript{2}]\textsubscript{2} with an $\alpha$-diimine ligand afforded [Rh(CO)\textsubscript{2}(Cl)\textsubscript{2}]$^-$ [Rh(CO)\textsubscript{2}(\alpha\text{-diimine})]$^+$ ion pairs,\textsuperscript{22,23} especially when an excess of [Rh(Cl)(CO)\textsubscript{2}]\textsubscript{2} was used. Our synthetic procedure did not give rise to such species.

When [Rh(Cl)(CO)(dmb)] was allowed to react with one equivalent of I\textsubscript{2}, a mixture of two products was formed, in both of which the dmb ligand is in an asymmetric environment according to $^1$H NMR. Since removal of the chloride ligand, using AgNO\textsubscript{3}, prior to oxidative addition of I\textsubscript{2} was found to result in a single, pure product, the products of the reaction of [Rh(Cl)(CO)(dmb)] with I\textsubscript{2} were not investigated further. NMR showed that the two pyridyl rings of the dmb ligand of [Rh(I)\textsubscript{2}(NO\textsubscript{3})(CO)(dmb)] are unequal.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.1.png}
\caption{Displacement ellipsoid plot of 1 (50\% probability level). The CH\textsubscript{2}Cl\textsubscript{2} molecule, present in the asymmetric unit, has been omitted for clarity. The methyl and carbonyl groups in the equatorial plane are disordered: The ligand position at C1 consists of 67.7(7)\% carbonyl and 32.3(7)\% methyl; the ligand position at C2 \textit{vice versa}.}
\end{figure}
Gradual addition of MeMgCl to [Rh(I)\textsubscript{2}(NO\textsubscript{3})(CO)(dmb)] caused the IR band due to the starting compound (2098 cm\textsuperscript{-1}) to disappear, while initially a band at 2058 cm\textsuperscript{-1} appeared which was in turn replaced by one at 2031 cm\textsuperscript{-1}. This indicates successive addition of two methyl groups. Single crystal X-Ray diffraction studies (vide infra) revealed the structure to be that depicted in Figure 6.1.

Addition of iPrMgCl to [Rh(I)\textsubscript{2}(NO\textsubscript{3})(CO)(dmb)] gave the corresponding orange-brown diisopropyl-rhodium species [Rh(iPr)\textsubscript{2}(I)(CO)(dmb)] (2) The v(CO) vibration has shifted to lower wavenumbers (2021 cm\textsuperscript{-1}), in line with the higher σ-donating strength of the isopropyl group, compared to the methyl ligand. Although Rh–iPr complexes are known,\textsuperscript{26–29} 2 is to our knowledge the first diisopropyl–rhodium complex. Table 6.1 presents all vibrational (IR, resonance Raman) data for complexes 1 and 2.

### Table 6.1 Vibrational data for complexes 1 and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR\textsuperscript{a} v(CO)\textsuperscript{b} resonance Raman\textsuperscript{c} (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(Me)\textsubscript{2}(I)(CO)(dmb)] (1)</td>
<td>2031 1621, 1560, 1492, 1322, 1284, 1030, 564, 526</td>
</tr>
<tr>
<td>[Rh(iPr)\textsubscript{2}(I)(CO)(dmb)] (2)</td>
<td>2021 1621, 1560, 1492, 1326, 1276, 1033, 570, 523, 234</td>
</tr>
<tr>
<td>dmb</td>
<td>– 1606, 1561, 1486, 1315, 1290, 1034, 236\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}in THF at room temperature; \textsuperscript{b}in cm\textsuperscript{-1}; \textsuperscript{c}in KNO\textsubscript{3}; \textsuperscript{d}selected Raman bands observed on 514.5 nm excitation of the ligand dispersed in a KNO\textsubscript{3} pellet.

#### 6.4.2 Crystal structure of cis-[Rh(Me)\textsubscript{2}(I)(CO)(dmb)] (1)

Table 6.2 lists the most important bond lengths and angles of 1, while Figure 6.1 shows a molecular The coordination environment of the Rh centre is distorted octahedral. The equatorial positions are occupied by the dmb ligand, a methyl and a carbonyl group, while an iodide and methyl group are in the axial ones. The dmb ligand is essentially planar with N–Rh bond lengths of 2.124(2) and 2.144(3) Å. The N–Rh–N angle of 76.76(9)° is significantly smaller than the perfect octahedral angle of 90°. The Rh–I bond length (2.7936(3) Å) is similar to that in [Rh(Cl)(I)(CH\textsubscript{2}I)(CO)(PET\textsubscript{3})\textsubscript{2}] (2.803 Å),\textsuperscript{30} and also to that of the isoelectronic complexes trans, cis-[Ru(I)(CH\textsubscript{3})(CO)\textsubscript{2}(iPr–DAB)] (2.7998(9) Å),\textsuperscript{31} but slightly shorter than that of [Pd(I)(Me)\textsubscript{3}(bpy)] (2.834 Å).\textsuperscript{32} The axial Rh–CH\textsubscript{3} bond (2.102(3) Å) is significantly longer than the equatorial ones (1.933(4) and 2.014(3) Å), indicating that the axial Rh–CH\textsubscript{3} bond is weaker (for the methyl carbonyl disorder, see section 6.3). A similar situation was encountered for [Pt(Me)\textsubscript{4}(CH\textsubscript{x}–DAB)] where the axial and equatorial Pt–C bond lengths are 2.140(8) Å and 2.045(5) Å, respectively.\textsuperscript{15} In contrast, for [Pd(I)(Me)\textsubscript{3}(bpy)], the
axial and equatorial Pd–C bond lengths are similar (2.040 Å and 2.034/2.046 Å, respectively).  

Table 6.2 Important bond lengths (Å) and angles (°) of non-hydrogen atoms of 1. Esd in last digit in parentheses.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bonds</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh–I</td>
<td>2.7936(3)</td>
<td>I–Rh–N1</td>
<td>89.86</td>
</tr>
<tr>
<td>Rh–C1</td>
<td>1.933(5)</td>
<td>I–Rh–N2</td>
<td>90.93</td>
</tr>
<tr>
<td>Rh–C2</td>
<td>2.014(3)</td>
<td>I–Rh–C1</td>
<td>92.20</td>
</tr>
<tr>
<td>Rh–C3</td>
<td>2.103(4)</td>
<td>I–Rh–C2</td>
<td>92.87</td>
</tr>
<tr>
<td>Rh–N1</td>
<td>2.144(2)</td>
<td>I–Rh–C3</td>
<td>179.56</td>
</tr>
<tr>
<td>Rh–N2</td>
<td>2.124(3)</td>
<td>N1–Rh–C1</td>
<td>101.54</td>
</tr>
<tr>
<td>Dmb</td>
<td></td>
<td>Torsion Angle (°)</td>
<td></td>
</tr>
<tr>
<td>N1–C4–C10–N2</td>
<td>1.0(4)</td>
<td>N2–Rh–C2</td>
<td>96.61</td>
</tr>
</tbody>
</table>

Figure 6.2 Absorption spectra of 1 (dotted) and 2 (drawn) in THF.

6.4.3 Electronic absorption and resonance Raman (rR) spectra

Figure 6.2 depicts the absorption spectra of 1 and 2 in THF. The spectra of both complexes show the dmb intraligand band at 295 nm as well as an absorption band at ca. 370 nm. The negative solvatochromism ($\Delta v = v($MeCN$) - v($toluene$) = 2.2 \times 10^3$ cm$^{-1}$) indicates that the transition belonging to the lowest-energy absorption band has strong charge transfer
character. In order to characterize these electronic transitions, rR spectra were recorded by excitation into these bands (Figure 6.3, Table 6.1).

![Resonance Raman spectra](image)

Figure 6.3 Resonance Raman spectra of (A) 1 ($\lambda_{\text{exc}} = 457.9$ nm) at room temperature and (B) 2 ($\lambda_{\text{exc}} = 457.9$ nm) at 90K in KNO$_3$. Asterisks denote nitrate bands.

The merit of the rR technique is based on the fact that those vibrations show a high Raman intensity that are coupled to the allowed electronic transition which is excited.\(^\text{33}\) For comparison, the Raman spectrum of the free ligand was recorded under the same conditions. The resonance enhanced vibrations for both 1 and 2 can all be assigned to dmb ligand vibrations, although the intensities of the resonance Raman bands of the complexes differ from those of the free ligand. This difference is due to the fact that in resonance Raman the intensity of a particular band is determined by the distortion of the compound in the excited state along the normal coordinate of that vibration, whereas the change in polarizability determines the intensity of a normal Raman band. The observation of resonance enhanced dmb vibrations implies the involvement of this ligand in the electronic transition belonging to the absorption band into which excitation takes place. The CO stretching frequency is not resonance enhanced, which implies that the charge density on the central metal atom is not affected by the electronic transition hence ruling out an MLCT assignment. No alkyl ligand vibrations are resonance enhanced which makes Sigma-Bond-to-Ligand Charge Transfer (SBLCT) character unlikely. Taking this into account, the lowest-energy absorption band most probably belongs to a Halide-to-Ligand Charge Transfer XLCT ($X = I$) transition. A
similar character of the lowest-energy electronic transition was found for [Re(I)(CO)$_3$(α-diimine)],$^{34}$ [Ru(I)(Me)(CO)$_2$(α-diimine)],$^{31}$ and [Pt(I)(Me)$_3$(iPr–DAB)].$^{7}$

6.4.4 Photochemistry

Both 1 and 2 are photoreactive in solution at room temperature. In order to study the primary photochemical step, THF solutions of 1 and 2 containing an excess of the spin-trap nitrosodurene, were irradiated in situ in an EPR spectrometer using a mercury lamp and suitable cutoff filters. Figure 6.4 presents the EPR spectrum obtained on irradiation ($\lambda_{irr}>435$ nm) of a THF solution of 2 containing an excess of nitrosodurene, as well as the PEST Winsim$^{35}$ simulated spectrum.

![EPR spectra](image.png)

Figure 6.4 Experimental (top) and simulated (bottom) EPR spectra obtained on irradiation ($\lambda_{irr}>435$) of 2 in a THF solution containing an excess of nitrosodurene.

The complicated spectrum indicates that both the metal fragment radical and the alkyl radical are trapped by nitrosodurene. Irradiation in the presence of an excess of PPh$_3$, used previously to trap the metal fragment selectively,$^{36}$ did not result in any observable EPR signal. The best fit is obtained by assuming the presence of a small amount of a third EPR active species (probably free nitrosodurene radical), in addition to the nitrosodurene (nd) trapped isopropyl and metal fragment radicals. The hyperfine splitting constants for nd–iPr$^*$ derived from the fitting procedure are $a_N = 13.59$ G and $a_H = 6.80$ G, in agreement with
literature values of 13.8 G and 6.7 G, respectively.\(^{37}\) The fitted hyperfine constants for the nd trapped metal fragment are \(a_N = 16.66\) G (nd), \(a_{\text{Rh}} = 1.19\) G and \(a_N = 2.16\) G (dmb). Due to the large linewidth of the latter radical (5.8 G) these last two splitting constant values are not very reliable. The fact that these values are small indicates that the electron spin is mainly located on the nd nitrogen atom.

Complex 1 does not show any radical formation under these circumstances, but shorter wavelength irradiation (\(\lambda_{\text{irr}}>335\) nm) does give rise to EPR detectable signals. In all cases, the photochemical reaction is not very efficient, with estimated quantum yields less than 0.01. On lowering the temperature, the efficiency is even much lower.

An XLCT excited state generally does not result in photochemical bond homolysis. Hence, the observed photoreaction must occur after crossing from the optically occupied electronic state to a reactive one. Of the excited states known to give rise to bond homolysis, the SBLCT state is the most likely candidate. Similar XLCT to SBLCT crossings were found for [Ru(I)(R)(CO)\(_2\)(iPr-DAB)] (R = iPr, Bz).\(^{38,39}\) In general, the energy of the transition metal to carbon bond of a metal–alkyl complex increases with increasing \(\sigma\) donor strength of the alkyl group, decreasing the energy of the SBLCT-state. In the complexes under study, the iPr group is the stronger \(\sigma\) donor. This explains that radical formation occurs at lower-energy irradiation for 2 than in the case of 1.

### 6.5 References


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CHAPTER 7

An Experimental and Theoretical Study of the Electronic Transitions and Emission Properties of \([\text{Pt}(I)(\text{CH}_3)_3(\text{iPr-DAB})]\), \([\text{Pt}((\text{CH}_3)_4(\alpha\text{-diimine}))\] and \([\text{Pt}(\text{SnPh}_3)_2(\text{CH}_3)_2(\text{iPr-DAB})]\)

7.1 Abstract

This chapter reports the results of a combined spectroscopic (UV/Vis, resonance Raman), emission and theoretical study of [Pt(I)(CH₃)₃(iPr-DAB)] (iPr-DAB = N,N-diisopropyl-1,4-diaza-1,3-butadiene), [Pt(CH₃)₄(R-DAB)] (R = alkyl or aryl), [Pt(CH₃)₄(α-diimine)] (α-diimine = tBu-Pyc, tmphen), and [Pt(SnPh₃)₂(CH₃)₂(iPr-DAB)]. The difference in character between the Halide-to-Ligand Charge Transfer (XLCT; X = I) transition of the first complex and the Sigma-Bond-to-Ligand Charge Transfer (SBLCT) transitions of the others, is clearly established by resonance Raman (rR) spectroscopy. DFT MO calculations confirm the assignment of the frontier orbitals and lowest-energy electronic transitions, and support the interpretation of the rR spectra. Furthermore, all complexes emit at low temperatures, with excited state lifetimes strongly depending on the character and reactivity of the lowest excited state.

7.2 Introduction

The [Pt(CH₃)₄(α-diimine)] complexes have been studied in some detail, ever since they were first reported in 1972.¹ These investigations included the reactions of these complexes with acids,² methyl group transfer reactions and reductive eliminations,³ and, most importantly for this study, their photoreactivity.⁴⁻⁸ This photosensitivity was already mentioned in the first paper,¹ and was later shown to involve a homolytic Pt–Cₐx bond splitting reaction from a triplet excited state. This was concluded from the results of EPR,⁷,⁸ CIDNP studies,⁴,⁵ triplet quenching,⁴,⁵ product analysis,⁶ and, more recently, FT-EPR measurements.⁹ This photoreactivity arises from the special character of the HOMO, which, according to DFT MO calculations is a σ(Me–Pt–Me) orbital, consisting of the antisymmetric combination of the axial methyl ligand orbitals, and only a small contribution from a platinum π orbital.⁶ Since the LUMO mainly consists of the lowest π* orbital of the α-diimine, the lowest-energy electronic transition has σ→π* or Sigma-Bond-to-Ligand Charge Transfer (SBLCT) character. This transition removes electron density from an already weak σ(Pt–Cₐx) bond, which renders these complexes very photoreactive.
Thus far, the emission properties of the [Pt(CH$_3$)$_4$(α-diimine)] complexes have received much less attention than those of other d$^6$ transition metal complexes, with lowest SBLCT excited states,\textsuperscript{10,11} such as [Re(R)(CO)$_3$(α-diimine)] (R = alkyl, metal fragment),\textsuperscript{12-15} and [M(L$_1$)(L$_2$)(CO)$_2$(α-diimine)] (M = Ru, Os; L$_1$, L$_2$ = e.g. CH$_3$, SnPh$_3$, Mn(CO)$_5$, RuCp(CO)$_2$, etc.).\textsuperscript{16-20} In the case of the Ru and Os complexes, the HOMO is a σ(L$_1$–M–L$_2$) orbital, and the lowest-energy transition has again SBLCT character.\textsuperscript{16,18} The SBLCT states of these complexes are reactive at room temperature, but stable at low temperature. Under the latter conditions, the excited state of these complexes can be extremely long lived, up to 1.1 ms for [Ru(SnPh$_3$)$_2$(CO)$_2$(dmb)] (dmb = 4,4’-dimethyl-2,2’-bipyridine).\textsuperscript{16,19}

In this chapter, the electronic absorption, resonance Raman and emission spectra of [Pt(I)(CH$_3$)$_3$(iPr–DAB)] (1), [Pt(CH$_3$)$_4$(α-diimine)] (2a–g) and of the novel complex [Pt(SnPh$_3$)$_2$(CH$_3$)$_2$(iPr–DAB)] (3) (iPr–DAB = N,N-diisopropyl-1,4-diaza-1,3-butadiene) are presented. The variety of α-diimine ligands in the complexes [Pt(CH$_3$)$_4$(diimine)] is chosen to establish their electronic and steric influence on the excited states. Tmphen (3,4,7,8-tetramethyl-1,10-phenanthroline) is well known to provide highly luminescent complexes with rather long excited state lifetimes. This is mainly due to the rigidity of this diimine ligand. Furthermore it represents a relatively electron-rich ligand compared to the 1,4-diazabutadienes. The tBu-Pyca (pyridine-2-carbaldehyde-tert.-butylimine) ligand was established as an intermediate between the aliphatic DAB ligands and aromatic α-diimine ligands like bipyridine or phenanthroline.\textsuperscript{6} In addition, DFT MO calculations are performed to characterize the molecular orbitals and to assign the electronic transitions belonging to the UV/Vis absorption bands, as well as the vibrations observed in the resonance Raman spectra. It is shown that variation of the axial ligands going from 1 to 2 to 3 has a dramatic effect on the spectroscopic and excited state properties. Figure 7.1 presents the general structure of the complexes.

![Figure 7.1 Schematic structures of the complexes under study.](image-url)
7.3 Experimental

**Materials.** I$_2$ (Merck), SnCl$_3$ (Merck, zur Synthese), tmphen (3,4,7,8-tetramethyl-1,10-phenanthroline) were used as received. Solvents purchased from Acros (THF, hexane, dichloromethane, acetonitrile, 2-MeTHF) were dried on and distilled from the appropriate drying agent when necessary. Silica gel (kieselgel 60, Merck, 70–230 mesh) was dried and activated by heating in vacuo at 160 °C overnight.

**Syntheses.** All syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. The complexes [Pt(CH$_3$)$_4$(R-DAB)] (2a–e),$^8$ [Pt(CH$_3$)$_4$(tBu-Pyca)] (2f),$^8$ [Pt(CH$_3$)$_2$]$_2$(iPr-DAB)],$^8$ as well as N,N'-diisopropyl-1,4-diazabutadiene (iPr-DAB),$^{21}$ were prepared according to literature procedures.

[Pt(I)$_2$(CH$_3$)$_2$(iPr-DAB)]. An excess of I$_2$ was added to a solution of [Pt(CH$_3$)$_2$]$_2$(iPr-DAB)] in CH$_2$Cl$_2$. Evaporation of the solvent and subsequent washing with pentane yielded the product as a dark brown powder in 60% yield. $^1$H NMR (CDCl$_3$): $\delta$: 1.55 (d, $^3J = 6.6$ Hz, 12H, CH(C$_3$)$_2$); 2.24 (s, $^3J = 73.1$ Hz, 6H, Pt-CH$_3$); 4.63 (septet, $^3J = 6.6$ Hz, 2H, CH(CH$_3$)$_2$); 8.53 (s, $^3J = 30.9$ Hz, 2H, imine H) ppm.

[Pt(I)(CH$_3$)$_3$(iPr-DAB)] (1) was prepared by oxidative addition of CH$_3$I to [Pt(CH$_3$)$_2$]$_2$(iPr-DAB)] in near-quantitative yield.$^{222}$ $^1$H NMR (CDCl$_3$): $\delta$: 0.66 (s, $^3J = 72.6$ Hz, 3H, Pt-Me$_a$); 1.42 (s, $^3J = 70.2$ Hz, 6H, Pt-Me$_e$); 1.41 (d, $^3J = 6.6$ Hz, 6H, iPr–DAB CH$_2$); 1.54 (d, $^3J = 6.6$ Hz, 6H, CH(CH$_3$)$_2$); 4.64 (septet, $^3J = 6.6$ Hz, 2H, CH(CH$_3$)$_2$); 8.61 (s, $^3J = 30.9$ Hz, 2H, imine H) ppm.

[Pt(CD$_3$)$_4$(iPr-DAB)] (2b) was prepared from CD$_3$Li, CD$_3$I and [Pt(Cl)$_2$]$_2$(μ-SMe$_2$)$_2$, according to the same procedure as [Pt(CH$_3$)$_2$]$_2$(iPr-DAB)].$^8$ $^1$H NMR (CD$_2$Cl$_2$): $\delta$: 1.35 (d, $^3J = 6.6$ Hz, 12H, CH(CH$_3$)$_2$); 4.56 (septet, $^3J = 6.6$ Hz, 2H, CH(CH$_3$)$_2$); 8.63 (s, $^3J = 31.5$ Hz, 2H, imine H) ppm.

[Pt(CH$_3$)$_4$(tmphen)] (2g) was prepared according to the same procedure as [Pt(CH$_3$)$_2$]$_2$(iPr-DAB)].$^8$ $^1$H NMR (C$_6$D$_6$): $\delta$: 0.39 (s, $^3J = 44$ Hz, 3H, Pt–Me$_a$); 1.97 (s, $^3J = 72.6$ Hz, 6H, Pt–Me$_e$); 1.69 (s, 6H, tmphen 4,7-CH$_3$); 1.89 (s, 6H, tmphen 3,8-CH$_3$); 7.41 (s, 2H, tmphen H 5,6); 9.01 (s, $^3J = 15.3$ Hz, 2H, tmphen H 2,9) ppm.

[Pt(SnPh$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] (3). A setup consisting of two two-necked Schlenk vessels connected by a G3 glass frit, was assembled. Water was rigorously removed by heating under vacuum. One Schlenk vessel was charged with 106 mg [Pt(I)$_2$(CH$_3$)$_2$(iPr-DAB)] and the other with a solution of 162 mg SnCl$_3$ in THF. The latter solution was freeze-pump-thaw degassed three times, after which THF was added to the platinum compound. After addition of an excess of NaK alloy to the brownish solution of [Pt(I)$_2$(CH$_3$)$_2$(iPr-DAB)], this solution turned purple and later brown-yellow. This extremely air-sensitive intermediate was filtered over a G3 glass filter into the solution of
Chapter 7. Electronic Transitions and Emission Properties of Pt(IV)-diimine complexes

SnClPh₃, which turned blue-green immediately. Evaporation of the solvent yielded a green solid, which was purified using column chromatography (activated silica, CH₂Cl₂/hexane gradient elution). The desired blue complex eluted in the first fraction. The second fraction contained a brown-red compound of unclear composition. FAB-MS; m/z: (M⁺ not detected), 716 (M⁺ – SnPh₃). UV/Vis (toluene); λₘₐₓ: 351, 657 nm. ¹H NMR (CD₂Cl₂): δ: 0.94 (d, J₁ = 6.6 Hz, 12H, CH(CH₃)₂), 1.34 (s, J₂Pₗ-H = 67.8 Hz, J₃Sn-H = 23.4 Hz, 6H, Pt–CH₃) 4.67 (sept, J₃ = 6.6 Hz, 2H, CH(CH₃)₂), 7.25 (m, 9H, m/p-SnC₆H₅), 7.29 (m, 6H, o-SnC₆H₅), 8.44 (m, J₄Sn-H = 29.1 Hz, 37.2 Hz, 2H, imine H) ppm.

Spectroscopic Measurements. All spectroscopic measurements were performed under a nitrogen atmosphere. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrophotometer, and electronic absorption spectra on Varian Cary 4E and Hewlett-Packard 8453 spectrophotometers. NMR spectra were recorded on a Varian Mercury 300 (300.13 MHz and 75.46 MHz for ¹H and ¹³C, respectively) spectrometer. Resonance Raman spectra of the complexes dispersed in KNO₃ pellets were recorded on a Dilor XY spectrometer equipped with a Wright Instruments CCD detector, using a Spectra Physics 2040E Ar⁺ and Coherent CR490 and CR590 dye lasers (with Coumarin 6 and Rhodamine 6G dyes) as the excitation sources. Nanosecond time-resolved electronic absorption and emission spectra were obtained with Spectra Physics GCR3 Nd:YAG and Coherent Infinity XPO excitation sources and an OMA detection system, described previously.²⁴

Computational Details. The iPr–DAB ligand was simplified to Me–DAB during the calculation of vibrational frequencies, while the SnPh₃ moiety was replaced by SnH₃ in all calculations. The ground state electronic structures of [Pt(CH₃)₄(iPr–DAB)] (2a), [Pt(SnH₃)₂(CH₃)₂(iPr–DAB)] and [Pt(I)(CH₃)₃(iPr–DAB)] (1) complexes were calculated by density functional theory (DFT) methods using the ADF1999²⁵²⁶ program package, while Gaussian 98²⁷ was used for the calculations of the vibrations. The lowest-energy electronic transitions of the closed shell complexes were calculated by time-dependent DFT methods using the ADF-RESPONSE²⁸ and G98 programs.

Within Gaussian 98, Dunning’s polarized valence double ζ basis sets²⁹ were used for C, N and H atoms and the effective quasi relativistic effective core pseudopotentials and corresponding optimized set of basis functions³⁰³¹ for Pt, I and Sn. In these calculations, the hybrid Becke’s three parameter functional with the Lee, Yang and Parr correlation functional (B3LYP)³² were used.

Within the ADF program, Slater type orbital (STO) basis sets of triple ζ quality with polarization functions for Pt and double ζ with polarization functions for remaining atoms were employed. The inner shells were represented by a frozen core approximation, viz. 1s for C, N, 1s–3d for Pt, 1s–4d for I, and 1s–4p for Sn were kept frozen. The following density functionals were used within ADF: a local density approximation (LDA) with VWN parametrization of electron gas data or a functional including Becke’s gradient correction³³ to the local exchange expression in conjunction with Perdew’s gradient correction³⁴ to the LDA expression (BP). The scalar relativistic (SR) zero order
regular approximation (ZORA) was used within this study. The Adiabatic Local Density Approximation (ALDA), ignoring the frequency dependence, was used in post-SCF time-dependent DFT calculations.\textsuperscript{28}

The calculations on [Pt(CH\textsubscript{3})\textsubscript{4}(R-DAB)] (2) and [Pt(SnH\textsubscript{3})\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}(R-DAB)] were performed in constrained C\textsubscript{2v} symmetry, with the z-axis coincident with the C\textsubscript{2} symmetry axis. The R-DAB ligand and the C atoms of the equatorial CH\textsubscript{3} groups are located in the yz plane and the SnH\textsubscript{3}/CH\textsubscript{3} axial ligands lie on the x axis. Calculations on [Pt(I)(CH\textsubscript{3})\textsubscript{3}(R-DAB)] (1) were performed in constrained C\textsubscript{s} symmetry, with the z-axis bisecting the DAB ligand as above.

### 7.4 Results and Discussion

#### 7.4.1 Syntheses

Figure 7.1 shows the compounds under study. The syntheses of [Pt(I)(CH\textsubscript{3})\textsubscript{3}(iPr-DAB)] (1) and [Pt(CH\textsubscript{3})\textsubscript{4}(\alpha-diimine)] (2a–g) are fairly straightforward and proceed according to literature methods.\textsuperscript{8,22,23} The synthesis of [Pt(SnPh\textsubscript{3})\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}(iPr-DAB)] (3), on the other hand, is not trivial. Attempts to react [Pt(I)\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}(iPr-DAB)] with LiSnPh\textsubscript{3} resulted in decomposition. Instead [Pt(I)\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}(iPr-DAB)] was reduced using NaK alloy to yield a highly reactive intermediate, which was allowed to react with two equivalents of SnClPh\textsubscript{3}. Although several other organometallic Pt(IV) complexes with a Pt–Sn bond are known,\textsuperscript{35–38} only a few compounds with a trinuclear Sn–Pt–Sn bonded system have been reported.\textsuperscript{39,40}

#### 7.4.2 Absorption spectra and MO calculations

Complexes 2 and 3 absorb in the visible region, whereas 1 absorbs only at higher energy (Table 7.1, Figure 7.2). The assignments of the lowest-energy absorption bands are based in part on DFT MO-calculations on complexes 1, 2a and on [Pt(SnH\textsubscript{3})\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}(iPr-DAB)] which serves as a model compound for 3. The results of these calculations are collected in Tables 7.2–7.6.

The frontier orbital characters of complex 1 are clearly different from those of the other complexes. The highest occupied MOs are formed by a set of almost degenerate orbitals (27a'' and 37a') which both have p\textsubscript{\pi} (I) character (Table 7.2). The lower lying occupied orbital
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36 a' is a σ(I-Pt-CH₃) orbital, again mainly halide in character, while below this MO is a set of metal localized MOs (not shown). The LUMO (38a') has mainly (86%) π*(iPr-DAB) character. The two lowest-energy allowed (a'→a') transitions are therefore expected to have Halide-to-Ligand Charge Transfer (XLCT, X = I) character. This expectation is supported by time-dependent (TD) DFT calculations which show that these transitions have 98% 37a'→38a' and 98% 36a'→38a' character, respectively. The ADF/BP calculated (vacuum) transition energies of 0.98 eV and 1.94 eV are much too low to be accounted for by solvent effects. The G98/B3LYP calculated values of 1.64 eV and 2.35 eV are closer to the experimental ones (2.87 eV and ~3.87 eV in toluene), but still too low. This is not an uncommon result of DFT calculations on transition metal complexes possessing metal–halide bonds.⁴¹⁻⁴³

Table 7.1 Long wavelength absorption maxima.

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>λ_max (toluene) (nm)</th>
<th>λ_max (MeCN) (nm)</th>
<th>Δ (cm⁻¹) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Pt(I)(CH₃)₃(iPr-DAB)]</td>
<td>432</td>
<td>372</td>
<td>3734</td>
</tr>
<tr>
<td>2a</td>
<td>[Pt(CH₃)₄(iPr-DAB)]</td>
<td>531</td>
<td>479</td>
<td>2044</td>
</tr>
<tr>
<td>2b</td>
<td>[Pt(CD₃)₄(iPr-DAB)]</td>
<td>515</td>
<td>464</td>
<td>2134</td>
</tr>
<tr>
<td>2c</td>
<td>[Pt(CH₃)₄(tBu-DAB)]</td>
<td>520</td>
<td>471</td>
<td>2001</td>
</tr>
<tr>
<td>2d</td>
<td>[Pt(CH₃)₄(cHex-DAB)]</td>
<td>532</td>
<td>485</td>
<td>1822</td>
</tr>
<tr>
<td>2e</td>
<td>[Pt(CH₃)₄(Xyl-DAB)]</td>
<td>605</td>
<td>550</td>
<td>1653</td>
</tr>
<tr>
<td>2f</td>
<td>[Pt(CH₃)₄(tBu-Pyca)]</td>
<td>493</td>
<td>449</td>
<td>1988</td>
</tr>
<tr>
<td>2g</td>
<td>[Pt(CH₃)₄(tmphen)]</td>
<td>446</td>
<td>410</td>
<td>1969</td>
</tr>
<tr>
<td>3</td>
<td>[Pt(SnPh₃)₂(CH₃)₂(iPr-DAB)]</td>
<td>657</td>
<td>620</td>
<td>908</td>
</tr>
</tbody>
</table>

aν(MeCN)-ν(toluene); b from ref⁶

The results for [Pt(CH₃)₄(iPr-DAB)] (2a) are in line with those of earlier calculations on the [Pt(CH₃)₄(H-DAB)] model complex.⁶ Thus, the HOMO is mainly composed of the antisymmetric combination of the axial sp³(CH₃) orbitals and pₓ(Pt), while the LUMO mainly consists of the lowest π* orbital of the iPr-DAB ligand (see Figure 7.1 for the orientation of the axes). According to DFT calculations (Table 7.3), some mixing between σ and π* orbitals occurs in both HOMO and LUMO. The lowest-energy transition has 93% 13b₁→14b₁ (HOMO→LUMO) character according to TD DFT calculations (Table 7.4). In view of the characters of the orbitals involved, it can best be described as a Sigma-Bond-to-Ligand Charge Transfer (SBLCT) transition. The second allowed transition (91% 12b₁→14b₁) has
MLCT character. The calculated absorption maxima (623 and 386 nm, respectively, Table 7.4) are lower than the observed absorption maxima (531 and 326 nm in toluene, respectively), but this is expected in view of the solvatochromic behaviour of the absorption bands.

![Figure 7.2 UV/Vis absorption spectra of [Pt(I)(CH₃)₃(iPr-DAB)] (1, drawn), [Pt(CH₃)₄(iPr-DAB)] (2a, dashed) and [Pt(SnPh₃)₂(CH₃)₂(iPr-DAB)] (3, dotted) in THF at room temperature. The inset shows the complete spectrum of 3.](image)

<table>
<thead>
<tr>
<th>MO</th>
<th>E (eV)</th>
<th>Prevailing Character</th>
<th>Pt</th>
<th>I</th>
<th>Me₉ₓ</th>
<th>Me₉ᵦ</th>
<th>iPr–DAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unoccupied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38a'</td>
<td>−3.84</td>
<td>π⁺R–DAB</td>
<td>7(dₓᵧ); 1(pₓ)</td>
<td>6</td>
<td>1</td>
<td></td>
<td>86(π⁺)</td>
</tr>
<tr>
<td>Occupied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27a''</td>
<td>−4.75</td>
<td>I(pₓ) + Pt(dₓ)</td>
<td>6(dₓ)</td>
<td>91</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>37a'</td>
<td>−4.78</td>
<td>I(pₓ) + Pt(dₓ)</td>
<td>3(dₓᵧ)</td>
<td>94</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>36a'</td>
<td>−5.57</td>
<td>I(σ), Pt, Me(σ)</td>
<td>7(pₓ); 1(dₓ₂); 4(dₓᵧ)</td>
<td>59</td>
<td>20</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 7.3 ADF calculated one-electron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals of [Pt(CH$_3$)$_4$(iPr-DAB)] (2a) expressed in terms of composing fragments.

<table>
<thead>
<tr>
<th>MO</th>
<th>E (eV)</th>
<th>Prevailing Character</th>
<th>Pt</th>
<th>(Me)$_{ax}$</th>
<th>(Me)$_{eq}$</th>
<th>iPr-DAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unoccupied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14b$_1$</td>
<td>-3.35</td>
<td>$\pi^* R$-DAB + (Me)$_{ax}$</td>
<td>8 (d$_{ax}$); 1 (p$_x$)</td>
<td>14</td>
<td>77($\pi^*$)</td>
<td></td>
</tr>
<tr>
<td>Occupied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13b$_1$</td>
<td>-4.79</td>
<td>Me$_{ax}$ + Pt + $\pi^* R$-DAB</td>
<td>9 (p$<em>x$); 1 (d$</em>{xz}$)</td>
<td>73</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>9a$_2$</td>
<td>-5.48</td>
<td>d$_{pt}$ + $\pi^* R$-DAB</td>
<td>75 (d$_{xy}$)</td>
<td>8</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>21a$_1$</td>
<td>-5.71</td>
<td>d$<em>{pt}$ + Me$</em>{eq}$</td>
<td>53 (d$<em>{z^2}$); 22 (d$</em>{x^2-y^2}$)</td>
<td>17</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>12b$_1$</td>
<td>-5.93</td>
<td>d$_{pt}$ + R-DAB</td>
<td>71 (d$_{xz}$); 1 (p$_x$)</td>
<td>10</td>
<td>6</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 7.4 TD DFT calculated lowest-energy singlet excitation energies and observed absorption maxima for [Pt(CH$_3$)$_4$(iPr-DAB)] (2a).

<table>
<thead>
<tr>
<th>State</th>
<th>Composition</th>
<th>Calculated transition energy (eV)</th>
<th>$\lambda_{abs}$ (nm)$^a$</th>
<th>Calc. osc. strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$</td>
<td>93% (13b$_1$ $\rightarrow$ 14b$_1$)</td>
<td>1.99</td>
<td>623</td>
<td>531</td>
</tr>
<tr>
<td>$^1B_2$</td>
<td>94% (9a$_2$ $\rightarrow$ 14b$_1$)</td>
<td>2.26</td>
<td>549</td>
<td>n.o.$^b$</td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>91% (12b$_1$ $\rightarrow$ 14b$_1$)</td>
<td>3.21</td>
<td>386</td>
<td>326</td>
</tr>
</tbody>
</table>

$^a$Observed wavelength maximum in toluene at room temperature. $^b$not observed

The characters of the relevant MOs and calculated electronic transitions of [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] (which serves as a model for 3) are similar to those of 2a. A slightly stronger $\sigma$-$\pi^*$ mixing is present in the frontier orbitals (Table 7.5) of the former complex. Thus, the contribution of the lowest $\pi^*(iPr-DAB)$ orbital to the HOMO is 18%, compared to only 13% in the case of 2a. Similarly, the contribution of the axial ligands to the LUMO is 23% in the case of [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)], but only 14% for 2a. On the other hand, the delocalization in [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] is still significantly less than in the isoelectronic model complex [Ru(SnH$_3$)$_2$(CO)$_2$(H-DAB)]. In this latter complex the contributions of $\pi^*(iPr-DAB)$ to the HOMO and of SnH$_3$ to the LUMO are both 27%, according to DFT calculations. Recent calculations on [Ru(SnH$_3$)$_2$(CO)$_2$(iPr-DAB)] showed that this calculated difference is certainly not due to replacement of iPr-DAB by H-DAB in the former calculations. This decrease of delocalization, going from [Ru(SnH$_3$)$_2$(CO)$_2$(H-DAB)] to [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] is also responsible for the shift of the first absorption
band to lower energy, going from [M(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)] (M = Ru, Os) (523 and 497 nm in toluene, respectively) to complex 3 (657 nm in toluene). This effect is mainly due to stabilization of the HOMO by the strong $\sigma-\pi^*$ interaction in the former complexes.$^{18,19}$

Another consequence of the weaker $\sigma-\pi^*$ interaction for 3 is a lowering of the molar extinction coefficient from over $6.0 \times 10^3$ M$^{-1}$.cm$^{-1}$ in the case of the Ru/Os complexes to $1.1 \times 10^3$ M$^{-1}$.cm$^{-1}$ in the case of 3, which is in fact very similar to the extinction coefficients of the complexes 2.

The calculated maximum of the lowest allowed electronic transition of [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] (655 nm, Table 7.6) is the same as the observed absorption maximum of 657 nm of 3 in toluene. The second absorption band (observed at 351 nm in toluene for 3) seems to consist of three allowed transitions (Table 7.6) of very mixed character. The observed ratio of the extinction coefficients of 1:10 for the low and high energy absorptions respectively, fits very well with the calculated oscillator strengths. Employing the more electron rich tBu-Pyc a and tmphen ligands shifts the absorption maximum of the [Pt(CH$_3$)$_4$(α-diiimine)] complexes to higher energy in line with the higher $\pi^*$ level of these ligands.

**Table 7.5** ADF calculated one-electron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals of [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] expressed in terms of composing fragments.

<table>
<thead>
<tr>
<th>MO</th>
<th>E (eV)</th>
<th>Prevailing Character</th>
<th>Pt</th>
<th>SnH$_3$</th>
<th>Me</th>
<th>iPr-DAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>25a$_1$</td>
<td>-1.41</td>
<td>$d_n + \text{SnH}_3$</td>
<td>6 ($d_{z^2}$); 13 ($d_{x^2-y^2}$)</td>
<td>70</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>17b$_1$</td>
<td>-3.54</td>
<td>$\pi^* \text{R-DAB} + \text{SnH}_3$</td>
<td>5($d_{xy}$); 1 ($p_z$)</td>
<td>23</td>
<td>71($\pi^*$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16b$_1$</td>
<td>-4.87</td>
<td>$\text{SnH}_3 + \text{Pt} + \pi^* \text{R-DAB}$</td>
<td>10 ($p_z$); 6($d_{xy}$)</td>
<td>60</td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>11a$_2$</td>
<td>-6.18</td>
<td>$d_n + \pi^* \text{R-DAB}$</td>
<td>67 ($d_{xy}$);</td>
<td>5</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td>24a$_1$</td>
<td>-6.21</td>
<td>$d_n + \text{Me}$</td>
<td>50 ($d_{z^2}$); 23 ($d_{x^2-y^2}$)</td>
<td>18</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>18b$_2$</td>
<td>-6.57</td>
<td>$\pi \text{R-DAB} + d_n + \text{Me}$</td>
<td>12 ($d_{xy}$) 3 ($p_y$)</td>
<td>6</td>
<td>38</td>
<td>41</td>
</tr>
<tr>
<td>15b$_1$</td>
<td>-6.64</td>
<td>$d_n + \text{R-DAB}$</td>
<td>66 ($d_{z^2}$); 1 ($p_z$)</td>
<td>13</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>14b$_1$</td>
<td>-7.27</td>
<td>$\text{SnH}_3$</td>
<td>4 ($d_{xy}$)</td>
<td>84</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>22a$_1$</td>
<td>-7.43</td>
<td>$\text{SnH}_3$</td>
<td>2 ($s$); 1 ($d_{z^2}$)</td>
<td>87</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>
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Table 7.6 TD DFT calculated lowest-energy singlet excitation energies (eV) for [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)].

<table>
<thead>
<tr>
<th>State</th>
<th>Composition</th>
<th>Calculated energy (eV)</th>
<th>Calculated transition $\lambda_{\text{abs}}$ (nm)</th>
<th>Calc. osc. strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$</td>
<td>96% (16b$_1$ → 17b$_1$)</td>
<td>1.89</td>
<td>656</td>
<td>657</td>
</tr>
<tr>
<td>$^1B_2$</td>
<td>94% (11a$_2$ → 17b$_1$)</td>
<td>2.80</td>
<td>443</td>
<td>n.o.$^b$</td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>86% (15b$_1$ → 17b$_1$); 10% (14b$_1$ → 17b$_1$)</td>
<td>3.49</td>
<td>355</td>
<td>n.o.$^b$</td>
</tr>
<tr>
<td>$^1B_1$</td>
<td>68% (16b$_1$ → 25a$_1$); 20% (22a$_1$ → 17b$_1$)</td>
<td>3.85</td>
<td>322</td>
<td>351</td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>89% (14b$_1$ → 17b$_1$)</td>
<td>3.88</td>
<td>320</td>
<td>n.o.$^b$</td>
</tr>
<tr>
<td>$^1B_1$</td>
<td>79% (22a$_1$ → 17b$_1$); 14% (16b$_1$ → 25a$_1$)</td>
<td>3.98</td>
<td>311</td>
<td>n.o.$^b$</td>
</tr>
</tbody>
</table>

$^a$Observed absorption maximum for [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(iPr-DAB)] in toluene at room temperature.

$^b$Not observed

Figure 7.3 Resonance Raman spectra obtained by excitation into the lowest-energy absorption band of (A) [Pt(I)(CH$_3$)$_3$(iPr–DAB)] (1) ($\lambda_{\text{exc}}$ = 457.9 nm), (B) [Pt(CH$_3$)$_4$(cHx–DAB)] (2a) ($\lambda_{\text{exc}}$ = 488.0 nm), (C) [Pt(CD$_3$)$_4$(iPr–DAB)] (2b) and (D) [Pt(SnPh$_3$)$_2$(CH$_3$)$_2$(iPr–DAB)] (3) ($\lambda_{\text{exc}}$ = 595.6 nm) in KNO$_3$.

Asterisks denote NO$_3^-$ bands.
7.4.3 Resonance Raman spectra

In order to further characterize the electronic transitions and confirm their assignment, the resonance Raman (rR) spectra of the complexes 1, 2a–g and 3 were investigated. Such spectra, obtained by excitation into an allowed electronic transition, show resonance enhancement of the Raman intensity for those vibrations which are most strongly affected by that particular electronic transition. The complexes containing aliphatic R–DAB ligands are especially suited for this study, since the simple structure of these ligands simplifies the rR spectra of their complexes. In order to assist in the assignment of the Raman bands, the vibrational frequencies of [Pt(I)(CH₃)₃(Me–DAB)], [Pt(CH₃)₄(Me–DAB)] and [Pt(SnH₃)₂(CH₃)₂(Me–DAB)] were calculated using the Gaussian 98 program package (Table 7.7).

The three types of complexes show different rR spectra (Figure 7.3). The main feature of the rR spectrum of [Pt(I)(CH₃)₃(iPr–DAB)] (1) (Figure 7.3A) is the presence of only one strong band at 1597 cm⁻¹. According to the present DFT calculations and in agreement with results for the related complex [Ru(I)(CH₃)(CO)₂(iPr–DAB)], this band is assigned to νₛ(CN) of the iPr–DAB ligand. The calculated wavenumber of this frequency of 1647 cm⁻¹ is about 3% too high, which is a usual deviation for DFT calculated frequencies using B3LYP potentials and double ζ basis sets. A scaling factor of 0.961 was recommended in literature.

For all complexes, this νₛ(CN) vibration has a CC-stretching motion contribution, similar to that shown for 3 in Figure 7.4. The spectrum shows a few other, much weaker, bands. Of these, the 1226 cm⁻¹ band (calculated 1279 cm⁻¹) can be ascribed to an umbrella type deformation of the axial methyl group on the basis of the calculations, while the band at 553 cm⁻¹ belongs to the symmetric C(eq)–Pt–C(eq) stretching motion.

No Pt–I stretching vibration was observed, in contrast to the case of [Re(I)(CO)₃(iPr–DAB)], where ν(Re–I) was found to be resonantly enhanced by the XLCT transition. The only vibration with ν(Pt–I) character was calculated at 121 cm⁻¹ for 1. In this region, rR bands are hard to detect, due to scattered laser light and the presence of a nitrate vibration. Thus, ν(Pt–I) may have escaped detection. For other complexes ν(Pt–I) was observed, viz. at 142 cm⁻¹ for the mixed valence complex [Pt(I)₃(diaminobenzene)]₄⁹ at ca 130 cm⁻¹ for linear chain mixed valence M(II)/Pt(IV) (M = Ni, Pt) complexes,⁵₀,⁵¹ and also at ca 130 cm⁻¹ for the [Pt(CH₃)₃(I)(L)₂] complexes, where L denotes a phosphine ligand. No bands are observed above 2000 cm⁻¹. These results are in agreement with the XLCT (X = I) character of the electronic transition.
Table 7.7 Calculated (unscaled) and observed resonance Raman bands.¹

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu_s(\text{CN}) )</th>
<th>( \delta_s(\text{CH}<em>3)</em>{ax} )</th>
<th>( \nu_s(\text{PtC})_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pt}(\text{I})(\text{CH}_3)_3(\text{Me-DAB})] ) (calc.)</td>
<td>1647</td>
<td>1279</td>
<td>578</td>
</tr>
<tr>
<td>([\text{Pt}(\text{I})(\text{CH}_3)_3(\text{iPr-DAB})] ) (I)</td>
<td>1597</td>
<td>1226</td>
<td>572</td>
</tr>
<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{Me-DAB})] ) (calc.)</td>
<td>1602</td>
<td>1213</td>
<td>555</td>
</tr>
<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{iPr-DAB})] ) (2a)</td>
<td>2731</td>
<td>2320</td>
<td>1564</td>
</tr>
<tr>
<td>([\text{Pt}(\text{CD}_3)_4(\text{Me-DAB})] ) (calc.)</td>
<td>1590</td>
<td>923</td>
<td>454</td>
</tr>
<tr>
<td>([\text{Pt}(\text{CD}_3)_4(\text{iPr-DAB})] ) (2b)</td>
<td>2478</td>
<td>1802</td>
<td>1567</td>
</tr>
<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{tBu-DAB})] ) (2c)</td>
<td>2759</td>
<td>2325</td>
<td>1585</td>
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<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{cHx-DAB})] ) (2d)</td>
<td>2720</td>
<td>2334</td>
<td>1548</td>
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<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{Xyl-DAB})] ) (2e)</td>
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<td></td>
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<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{tBu-Pyca})] ) (2f)</td>
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<td></td>
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<tr>
<td>([\text{Pt}(\text{CH}_3)_4(\text{tmphen})] ) (2g)</td>
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</tr>
</tbody>
</table>

\( \nu_s(\text{CN}) + 2 \delta_s(\text{CH}_3)_{ax} \)

\( \nu_s(\text{CN}) \quad \delta_s(\text{CH}_3)_{ax} \quad \delta_s(\text{DAB}) \quad \delta_s(\text{DAB}) \)

<table>
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<tr>
<th>Complex</th>
<th>( \nu_s(\text{CN}) )</th>
<th>( \delta_s(\text{CH}<em>3)</em>{ax} )</th>
<th>( \delta_s(\text{DAB}) )</th>
<th>( \delta_s(\text{DAB}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pt}(\text{SnH}_3)_2(\text{CH}_3)_2(\text{Me-DAB})] ) (calc.)</td>
<td>1552</td>
<td>1410</td>
<td>979</td>
<td>839</td>
</tr>
<tr>
<td>([\text{Pt}(\text{SnPh}_3)_2(\text{CH}_3)_2(\text{iPr-DAB})] ) (3)</td>
<td>1475</td>
<td>1293</td>
<td>948</td>
<td>834</td>
</tr>
</tbody>
</table>

¹In the assignments the major contribution is mentioned, see text for more details; ²not observed; ³\( \nu_s(\text{CN}) \) and ring stretching motions observed at 1607, 1554, 1504, 1302 cm\(^{-1}\); ⁴\( \nu_s(\text{CN}) \) and ring stretching motions observed at 1625, 1564, 1482, 1302, 1263, 1248, 1157, 1077, 1025 cm\(^{-1}\); ⁵\( \nu_s(\text{CN}) \) and ring stretching motions observed at 1648, 1585, 1521, 1441, 1385, 1313, 1246 cm\(^{-1}\); ⁶Metal–ligand stretching and ligand deformation vibrations observed at 798, 746, 640, 581, 533, 511, 466 cm\(^{-1}\).

The rR spectra of \([\text{Pt}(\text{CH}_3)_4(\text{R-DAB})] \) (2a–d) show the same \( \nu_s(\text{CN}) \) vibration at 1550–1580 cm\(^{-1}\), the calculated value (1602 cm\(^{-1}\)) being again a few percent too high. The lower frequency of this vibration compared to that of I, is due to the π-backbonding to the R-DAB ligand. Since π*(R–DAB) is antibonding with respect to the CN bonds, occupation of this orbital in the ground state leads to a weakening of that bond and a decrease of its frequency. A further increase of the π-backbonding is observed in the rR spectra of 3 (\( \nu_s(\text{CN}) = 1475 \text{ cm}^{-1} \), vide infra), in agreement with the MO calculations (vide supra). The difference in character between the lowest-energy electronic transitions of 1 and 2 is evident from the
The rR spectrum of \([\text{Pt(SnPh}_3^3\text{)}_2(\text{CO})_2(i\text{Pr-DAB})]\) (3) shows, apart from \(v_s(\text{CN})\) (at 1475 cm\(^{-1}\)), a strong band at 1293 cm\(^{-1}\). According to the calculations it is an in plane \(\delta(\text{imine CH})\) mode, combined with \(v_s(\text{CN})\) and with a contribution from \(v(\text{CC})\) (See Figure 7.4). Recent rR measurements on the isoelectronic \([\text{M(SnPh}_3^3\text{)}_2(\text{CO})_2(i\text{Pr-DAB})]\) (M= Ru, Os)

![Schematic pictures of the displacements that belong to the two most resonance enhanced vibrations of Pt(SnPh3)2(CH3)2(iPr-DAB) (3), viz v_s(CN) (A) and δ(CH) (B); see text for details.](image-url)
complexes show exactly the same band.\textsuperscript{16,19} The calculated value of 1410 cm\textsuperscript{-1} for this $\delta$(CH) vibration deviates more than expected from the observed value. This is due to the fact that this vibration is very sensitive to the substituents on the nitrogen atoms of the DAB ligand. Recent calculations on [Ru(SnH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(R–DAB)] (R = Me, iPr) showed a change in calculated frequency of the above mentioned vibration from 1405 cm\textsuperscript{-1} to 1326 cm\textsuperscript{-1} going from R = Me to R = iPr.\textsuperscript{44} The 948 and 834 cm\textsuperscript{-1} bands correspond to ligand deformation bands. They were also found for the [M(SnPh\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr–DAB)] (M = Ru, Os) complexes, although more intense due to the stronger $\sigma$–$\pi^*$ interaction.\textsuperscript{16,19}

<table>
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<tr>
<th>#</th>
<th>Compound</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\Delta E_{abs-em}$ (cm\textsuperscript{-1})</th>
<th>$\tau$ (10\textsuperscript{2} ns)</th>
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<tbody>
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<td>1</td>
<td>[Pt(I)(CH\textsubscript{3})\textsubscript{3}(iPr–DAB)]</td>
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<td>550</td>
<td>8628</td>
<td>6.9</td>
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<tr>
<td>2a</td>
<td>[Pt(CH\textsubscript{3})\textsubscript{4}(iPr–DAB)]</td>
<td>468</td>
<td>775</td>
<td>8464</td>
<td>0.25</td>
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<tr>
<td>2c</td>
<td>[Pt(CH\textsubscript{3})\textsubscript{4}(tBu–DAB)]</td>
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<td>750</td>
<td>8218</td>
<td>0.35</td>
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<tr>
<td>2d</td>
<td>[Pt(CH\textsubscript{3})\textsubscript{4}(cHx–DAB)]</td>
<td>457</td>
<td>775</td>
<td>8979</td>
<td>0.44</td>
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<tr>
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<td>694</td>
<td>7850</td>
<td>1.8</td>
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<tr>
<td>2g</td>
<td>[Pt(CH\textsubscript{3})\textsubscript{4}(tmpphen)]</td>
<td>416</td>
<td>600</td>
<td>7371</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>[Pt(SnPh\textsubscript{3})\textsubscript{2}(CH\textsubscript{2})\textsubscript{2}(iPr–DAB)]</td>
<td>615</td>
<td>809</td>
<td>3899</td>
<td>12</td>
</tr>
</tbody>
</table>

### 7.4.4 Low Temperature Emission Spectra

Absorption and time-resolved emission spectra were recorded for all complexes in a 2-MeTHF glass at 90 K, under which conditions they are more or less photostable. The absorption bands are blue-shifted by about 20 nm compared to room temperature, due to the rigidochromic effect. Table 7.8 shows the absorption and emission maxima, as well as the emission lifetimes. First of all, [Pt(I)(CH\textsubscript{3})\textsubscript{3}(iPr–DAB)] (I) emits from its XLC T state with a lifetime of 6.9 $\mu$s, which is slightly longer than the XLC T emission lifetime of the related complex [Ru(I)(CH\textsubscript{3})(CO)\textsubscript{2}(iPr–DAB)] (1.8 $\mu$s),\textsuperscript{44} due to the higher emission energy.

Although [Pt(CH\textsubscript{3})\textsubscript{4}(bpy)] was reported to be non-emissive even in a glass,\textsuperscript{5} we found the [Pt(CH\textsubscript{3})\textsubscript{4}(\alpha\textendash diimine)] complexes to emit weakly. The emission lifetimes of the [Pt(CH\textsubscript{3})\textsubscript{4}(\alpha\textendash diimine)] complexes is quite short compared to those of other complexes with a lowest SBLCT state, such as [Ru(L\textsubscript{1})(L\textsubscript{2})(CO)\textsubscript{2}(\alpha\textendash diimine)], where L\textsubscript{1} and L\textsubscript{2} can be alkyl groups or metal fragments.\textsuperscript{16,17,19,20} For instance, the complex [Ru(CH\textsubscript{3})(SnPh\textsubscript{3})(CO)\textsubscript{2}(iPr–
DAB) emits at 715 nm with a lifetime of 32 μs in a glass at 80 K, whereas 2a emits at 775 nm with a lifetime of 25 ns. This difference is too large to be ascribed to an energy-gap-law effect, but can be due to two other factors: First of all, the complexes are not entirely photostable under the measurement conditions, as can be seen from a change of colour of the sample after the experiment. Secondly, the complexes are more distorted in their SBLCT states than the Ru ones. A measure for this distortion is the energy difference between the absorption and emission maxima which is e.g. 8464 cm$^{-1}$ for 2a but only 5974 cm$^{-1}$ for [Ru(CH$_3$)(SnPh$_3$)(CO)$_2$(iPr-DAB)].$^{16}$ A large distortion of the complex in its excited state leads to a large vibrational overlap of the excited state with the ground state, which shortens the excited state lifetime.$^{55,56}$ Employing the more rigid ligands tBu–Pyca or tmphen decreases the distortion of the complexes in the excited state. This, together with a higher emission energy, results in an increase of emission lifetime from 25 ns for 2a to 177 ns for 2f to 9.3 μs for 2g.

The complex [Pt(SnPh$_3$)$_2$(CH$_3$)$_2$(iPr–DAB)] (3) is not only completely photostable in a glass, but also much less distorted in its excited state ($\Delta E_{\text{abs-em}} = 3899$ cm$^{-1}$) than the complexes 2. This causes a dramatic increase in the low temperature excited state lifetime to
1.2 μs in spite of the low emission energy. For comparison, the analogous complex [Os(SnPh$_3$)$_2$(CO)$_2$(iPr-DAB)] has a longer excited state lifetime of 32 μs, but emits at higher energy (655 nm compared to 809 for 3).

7.5 References

Chapter 7. Electronic Transitions and Emission Properties of Pt(IV)-diimine complexes

22) Scott, J. D.; Puddephatt, R. J. *Organometallics* 1986, 5, 1538.
41) Záliš, S., personal communication.
Chapter 7. Electronic Transitions and Emission Properties of Pt(IV)-diimine complexes

44) Záliš, S., personal communication.
Influence of the Metal–Ligand Interaction and the Character of the Electronic Transitions on the Resonance Raman Spectra of $d^6$ Metal–Diimine Complexes

8.1 Abstract

This chapter presents the results of a resonance Raman (rR) study of $d^6$ transition metal $\alpha$-diimine complexes. The $\alpha$-diimine ligand employed is $N,N'$-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB) which has a relatively simple structure and hence few vibrations. This makes assignment of the vibrational spectra of complexes of this ligand easier. It is shown that with the help of DFT calculations the bands observed in the rR spectra, obtained by irradiation into the lowest-energy absorption band, can be assigned unambiguously. Comparison of the spectra show how factors such as metal–ligand interaction and electronic transition character affect the rR spectra and enables one to assess how rR spectra can be used to characterize electronic transitions.

8.2 Introduction

Most of the early experimental data on molecular vibrations were provided by Raman spectroscopy, but the development and use of this technique stagnated when commercial infrared spectrometers became available in the 1940s. The discovery of the laser as a powerful monochromatic light source and the development of sensitive detectors in the 1960s initiated the renaissance of Raman spectroscopy. In addition, contrary to the light sources used earlier, lasers and dye-lasers made the recording of so-called resonance Raman (rR) spectra viable.\textsuperscript{1-6} Such rR spectra show enhancement of intensity of some Raman bands when the frequency of the exciting light approaches that of a strongly allowed electronic transition. If, as is usually the case, the ground state is totally symmetric, only bands due to totally symmetric vibrations are resonantly enhanced. Additionally, the intensity of a rR band belonging to a certain vibration depends on the relative displacement of the potential energy curve of the excited state with respect to that of the ground state along the normal coordinate of that vibration. In other words, the intensities are highest for those vibrations, which are most strongly coupled to that particular electronic transition. Although absorption bands of molecules contain information about all the displaced normal modes, they normally show up as an unresolved envelope in condensed media when many modes are displaced. In contrast, rR 'excitation profiles' (EP), which represent the rR intensity of a specific vibration as a function of the
wavelength of excitation, provide instead information about the displacement of individual modes. EPs of many inorganic complexes were successfully analysed by Zink and others \textsuperscript{6,7} in terms of excited state distortions with the time-dependent theory of Lee, Tannor and Heller.\textsuperscript{8-10} Thus, rR spectra do not only provide the vibrational frequencies of a molecule in its ground state but also characterize its allowed electronic transitions by giving valuable information about the involvement of individual vibrations in these transitions.

For many years we have applied the rR technique to assign and characterize the low-energy electronic transitions of low-valent transition metal α-diimine complexes.\textsuperscript{11-16} The main aim of these studies was to determine the changes in structure caused by the electronic transitions and to relate these changes to the photochemical and photophysical behaviour of the complexes. However, most rR bands could only be assigned qualitatively, since a complete vibrational analysis of the complexes was too complicated at the time. Partly due to increasing computer processor speeds, quantum chemical calculations have recently improved to such an extent that they can now provide unambiguous assignments of vibrational spectra even for complicated systems.

In view of this development and in order to obtain comparative rR data of a series of d\textsuperscript{6} metal α-diimine complexes differing in their ground- and/or excited state bonding properties, we recorded the rR spectra of these complexes under the same conditions. All complexes under study (Figure 8.1) contain the same α-diimine ligand iPr-DA B (N,N'-diisopropyl-1,4-diaza-1,3-butadiene). This ligand was chosen since due to its simple structure it has relatively few vibrations. At the same time, DFT B3LYP calculations were performed on the free ligand and several (model) complexes.

![Figure 8.1 Schematic structures of ligand and complexes under study.](image)

This chapter shows that by thorough comparison of the rR spectra of these complexes in combination with the results of the DFT calculations, most rR bands can be assigned.
Furthermore, the influences of electronic transition character, and metal–ligand interaction on the rR spectra can be separated and understood.

8.3 Experimental Section

Materials. Triphenylphosphine (PPh₃, Aldrich), [W(CO)₆] (Strem), neutral alumina (Fluka) and AgNO₃ (Aldrich) were used as received. Solvents purchased from Acros (dichloromethane, pentane, tetrahydrofuran, toluene), were dried on and distilled from the appropriate drying agent.

Syntheses. All syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. N,N’-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB), [Ru(Cl)(R)(CO)₂(iPr-DAB)], [Ru(R)(SnPh₃)(CO)₂(iPr-DAB)], [Pt(R)(iPr-DAB)], [Pt(SnPh₃)(CH₃)₂(iPr-DAB)], [Ru{RuCp(CO)₂}(CO)₂(iPr-DAB)], [Re(PPh₃)(CO)₃(iPr-DAB)](NO₃) was prepared by stirring [Re(Br)(CO)₃(iPr-DAB)] with one equivalent of AgNO₃ and an excess of PPh₃ in CH₂Cl₂. Filtration, evaporation of the solvent and washing with pentane afforded the pure product in near quantitative yield. IR (THF): ν(CO): 2027, 1927, 1908 cm⁻¹. ¹H NMR (CDCl₃); δ: 1.50 (d, ³J = 6.6 Hz, 12H, CH(C₆H₅)₂), 4.22, (septet, ³J = 6.6 Hz, 2H, CH(CH₃)₂), 8.61 (s, 2H, imine H) ppm.

[W(CO)₄(iPr-DAB)] was prepared by refluxing [W(CO)₆] and 1.1 equivalent of iPr-DAB overnight in toluene. Flash column chromatography over neutral alumina yielded a mixture of product and starting compound, the latter of which was removed by sublimation (30 °C) in vacuo. IR (CH₂Cl₂); ν(CO): 2027, 1927, 1908 cm⁻¹. ¹H NMR (CDCl₃); δ: 1.50 (d, ³J = 6.6 Hz, 12H, CH(CH₃)₂), 4.22, (septet, ³J = 6.6 Hz, 2H, CH(CH₃)₂), 8.61 (s, 2H, imine H) ppm.

Spectroscopic Measurements. Resonance Raman spectra of the complexes dispersed in KNO₃ pellets were recorded on a Dilor XY spectrometer equipped with a Wright Instruments CCD detector, using Spectra Physics 2040E Ar⁺ laser in combination with Coherent CR490 and CR590 dye lasers (with Coumarin 6 and Rhodamine 6G dyes) as excitation sources under a 180° backscattering geometry. The pellet was spun in order to minimize thermal and photochemical decomposition. Data acquisition was controlled by Dilor Labspec 2.08 software. The spectra were calibrated using the Raman bands due to the symmetrical stretching and in plane bending vibrations of NO₃⁻ (at 1051 and 716 cm⁻¹, respectively)²₄ and corrected for baseline deviations using Grams software.

Computational Details. The ground state electronic structures were calculated by density functional theory (DFT) methods using the ADF1999²⁵,²⁶ and Gaussian 98²⁷ program packages. Gaussian 98²⁷ was used for the calculations of the vibrations.
Within Gaussian 98, Dunning's polarized valence double \( \zeta \) basis sets\(^{28} \) were used for C, N, O, Cl and H atoms and the quasirelativistic effective core pseudopotentials and corresponding optimized set of basis functions\(^{29} \) for W, Ru, Os, Pt and Sn. In these calculations, the hybrid Becke's three parameter functional with the Lee, Yang and Parr correlation functional (B3LYP)\(^{30} \) were used.

Within the ADF program, Slater type orbital (STO) basis sets of triple \( \zeta \) quality with 3d polarization functions for C and additional p functions for metals were employed. The inner shells were represented by a frozen core approximation, viz. 1s for C, N, O, 1s–2p for Cl, 1s–3d for Ru, 1s–4d for Os, 1s–4f for Pt and 1s–4p for Sn were kept frozen. The following density functionals were used within ADF: a local density approximation (LDA) with VWN parametrization of electron gas data or a functional including Becke's gradient correction\(^{31} \) to the local exchange expression in conjunction with Perdew's gradient correction\(^{32} \) to the LDA expression (BP). The scalar relativistic (SR) zero order regular approximation (ZORA) was used within this study.

The calculations on iPr–DAB, [W(CO)\(_4\) (Me–DAB)], [Pt(CH\(_3\))\(_4\) (Me–DAB)], [Pt(CD\(_3\))\(_4\) (Me–DAB)], [Pt(SnH\(_3\))\(_2\) (CH\(_3\))\(_2\) (Me–DAB)], [Ru(SnH\(_3\))\(_2\) (CO)\(_2\) (iPr–DAB)], [Ru(SnH\(_3\))\(_2\) (CO)\(_2\) (Me–DAB)] and [Os(SnH\(_3\))\(_2\) (CO)\(_2\) (Me–DAB)] were performed in constrained \( C_2 \) symmetry, with the z-axis coincident with the \( C_2 \) symmetry axis. The R–DAB ligand and the C atoms of the equatorial CO/CH\(_3\)/CD\(_3\)/groups are located in the yz-plane and the SnH\(_3\)/CH\(_3\)/CD\(_3\)/axial ligands lie on the x-axis. Calculations on [Ru(Cl) (CH\(_3\)/CD\(_3\)) (CO)\(_2\) (Me–DAB)] and [Ru(CH\(_3\)) (SnMe\(_3\)) (CO)\(_2\) (Me–DAB)] were performed in constrained \( C_4 \) symmetry, with the z-axis bisecting the DAB ligand as above.

### 8.4 Results and Discussion

In this section the Raman spectrum of the free iPr–DAB ligand and the rR spectra of several of its complexes are presented, assigned and discussed. The assignments of the rR bands are based on comparisons with literature data, and on the results of DFT calculations. Firstly, the Raman spectrum of free iPr–DAB is presented and assigned. The complexes to be discussed thereafter were selected as follows: [Re(PPh\(_3\)) (CO)\(_3\) (iPr–DAB)]\(^{1+} \) and [W(CO)\(_4\) (iPr–DAB)] are both characterized by MLCT transitions in the visible region, but the metal–\( \alpha \)-diimine interaction is stronger for the W(0) than the Re(I) complex. The effect of this difference in interaction on the rR spectra is the subject of the second part of this section. The third part is concerned with the complexes [Re(CH\(_3\)) (CO)\(_3\) (iPr–DAB)], [Ru(Cl)(R)(CO)\(_2\) (iPr–DAB)], [Ru(R)(SnPh\(_3\)) (CO)\(_2\) (iPr–DAB)] and [Pt(R)\(_4\) (iPr–DAB)] (R = CH\(_3\), CD\(_3\)) and deals with the influence of the introduction of methyl co-ligands on the rR spectra and character of
the CT transition. Finally, the fourth part of this section contains the rR spectra of the di- and trinuclear metal–metal bonded complexes \([\text{Ru(Cl)(SnPh}_3(\text{CO})_2(iPr-DAB)]\), \([\text{Re(Re(CO)}_5(\text{CO})_3(iPr-DAB)]\), \([\text{Pt(SnPh}_3(\text{CH}_3_2(iPr-DAB)]\), \([\text{M(SnPh}_3(\text{CO})_2(iPr-DAB)]\) (M = Ru, Os) and \([\text{Ru(RuCp(CO)}_2_2(\text{CO})_2(iPr-DAB)]\). In the subsequent conclusions section, the principal factors (\(\pi\)-backbonding, orbital delocalization and electronic transition character) that influence the rR spectra are discussed. Table 8.1 lists the main resonance enhanced rR bands of all complexes under study.

![Figure 8.2](image)

**Figure 8.2** The Raman spectrum of iPr-DAB in CH\(_2\)Cl\(_2\), \(\lambda_{\text{exc}} = 514.5\) nm. Asterisks denote solvent bands.

1. **The ligand N,N'-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB).**

   The Raman spectrum of iPr-DAB was obtained by excitation at 514.5 nm of the freshly sublimed free ligand in CH\(_2\)Cl\(_2\) solution, rather than dispersed in a KNO\(_3\) pellet, in order to prevent sublimation by the laser beam. Figure 8.2 displays the resulting Raman spectrum, with solvent bands denoted with asterisks (*). To assist the assignment, the vibrations of this ligand were calculated in constrained s-cis geometry. The main band is observed at 1636 cm\(^{-1}\) and is attributed to the symmetrical stretching vibration of the CN bonds, \(\nu_s(\text{CN})\). It is calculated about 3% too high (1693 cm\(^{-1}\)), but such a difference between calculated and observed frequencies is quite normal for DFT calculations with B3LYP functionals and double \(\zeta\) basis sets.\(^{33}\) A number of weaker bands are found, but these are not readily assigned with the help of the calculations.
### Table 8.1 Main bands in the rR spectra of several iPr-DAB complexes. Assignments include major contributions only, for details see text. Calculated values\(^a\) are between brackets.

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<th>(v_s(CN))</th>
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<th>(\delta(Me))</th>
<th>(\delta(DAB))</th>
<th>(\delta(MCO))</th>
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<td>958</td>
<td>832</td>
<td>606</td>
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</table>

\(^a\) iPr-DAB was simplified to Me-DAB, and SnPh\(_3\) was replaced by SnH\(_3\); \(^b\)[W(CO)\(_4\)(iPr-DAB)]; \(^c\)[Ru(SnH\(_3\))\(_2\)(CO)\(_2\)(iPr-DAB)]
(2) The influence of metal–ligand interaction

The iPr–DAB ligand has a low-lying $\pi^*$ orbital, while low-valent transition metal atoms have relatively high-lying filled metal $d$ orbitals. Because of this, the complexes formed between such a metal and a chelating iPr–DAB ligand possess low-energy Metal-to-Ligand Charge Transfer (MLCT) transitions. Such an MLCT transition affects the bonds and vibrations of iPr–DAB and to a lesser extent those of the co-ligands. Which vibrations are influenced by an MLCT transition depends on the strength of the metal–ligand interaction as will be shown by the rR spectra of two representative complexes.

![Figure 8.3 RR spectra of [Re(PPh$_3$)(CO)$_3$(iPr-DAB)]$^+$ (top, $\lambda_{exc} = 457.9$ nm) and [W(CO)$_4$(iPr-DAB)] (bottom, $\lambda_{exc} = 514.5$) in KNO$_3$. Asterisks denote NO$_3^-$ bands.](image-url)

[Re(PPh$_3$)(CO)$_3$(iPr-DAB)]$^+$. As the first example of a complex with a lowest MLCT transition [Re(PPh$_3$)(CO)$_3$(iPr-DAB)]$^+$ was selected rather than the well known complex [Re(Cl)(CO)$_3$(iPr-DAB)]. In the latter complex the chloride ligand orbitals participate in the highest filled orbitals, causing a deviation of the lowest-energy electronic transition from pure MLCT character. This is evidenced by the observation of $\nu$(Re–Cl) in the rR spectrum of this complex.$^{12,34}$ The rR spectrum of [Re(PPh$_3$)(CO)$_3$(iPr-DAB)]$^+$, obtained by excitation into its lowest-energy absorption band, only shows two resonantly enhanced Raman bands (Figure
8.3). The stronger one of these is found at 1557 cm\(^{-1}\) and is attributed to \(v_4(CN)\). It is \(ca.\) 80 cm\(^{-1}\) lower in frequency than observed for the free ligand, due to \(d_\pi(Re)\)-\(\pi^*(iPr-DAB)\) \(\pi\)-backbonding. This \(\pi^*\) orbital is antibonding with respect to the CN bonds, which explains the lowering of frequency of \(v_4(CN)\) in the ground state of the complex compared to the free ligand. The MLCT transition increases the electron density in the \(\pi^*(iPr-DAB)\) orbital even more. Hence, this transition affects the CN stretching vibration, leading to resonance enhancement of the Raman intensity for this vibration in the \(rR\) spectrum. The other resonantly enhanced band at 2025 cm\(^{-1}\) belongs to the in-phase symmetric vibration \(v_5(CO)\) of the three carbonyls.\(^{35}\) During the electronic transition the metal atom is oxidized, which decreases the metal–CO \(\pi\)-backbonding and leads to resonance enhancement of the CO stretching vibration.

\([W(CO)_4(iPr-DAB)]\). Going from Re(I) to W(0) the metal \(d\) orbital energy is raised, causing an increase of the metal\(\rightarrow\)iPr-DAB \(\pi\)-backbonding. In the \(rR\) spectrum (Figure 8.3) this is manifested by a lowering of frequency for \(v_3(CN)\) from 1557 to 1499 cm\(^{-1}\). The calculated value is 1531 cm\(^{-1}\) for \([W(CO)_4(iPr-DAB)]\). Since the metal atom is oxidized during the electronic transition, the in-phase symmetric mode of the carbonyls,\(^{36}\) \(v_5(CO)\), is again resonantly enhanced and observed at 2017 cm\(^{-1}\) (calculated at 2089 cm\(^{-1}\)). However, a number of extra Raman bands are observed for \([W(CO)_4(iPr-DAB)]\) (at 1147, 931, 847, 624, 480, 432 and 222 cm\(^{-1}\)), which are not present in the spectrum of the Re complex. With the aid of the DFT vibrational calculations these can be assigned. The band at 1147 cm\(^{-1}\) was observed at 1150 cm\(^{-1}\) for \([Mo(CO)_4(iPr-DAB)]\),\(^{37}\) and found to shift on \(^{15}\)N isotope substitution.\(^{38}\) It is assigned to a vibration which has combined \(\delta(CH)\) and \(v_5(CN)\) character. The former component is an in-plane symmetric motion of the two imine hydrogen atoms. The frequency of this vibration is very sensitive to the nature of the substituent on the N atoms of the diazabutadiene backbone, which was proven by vibrational calculations on \([W(CO)_4(R-DAB)]\) (\(R = \text{Me, iPr}\)) (\textit{vide infra}). For \(R = \text{Me,} \ \delta(CH)\) is calculated at 1409 cm\(^{-1}\), while the calculated value for \(R = \text{iPr}\) (1176 cm\(^{-1}\)) is much closer to the observed one (1147 cm\(^{-1}\)). The bands found at 931 and 847 cm\(^{-1}\) (calculated at 960 cm\(^{-1}\) and 830 cm\(^{-1}\) for \([W(CO)_4(iPr-DAB)]\)) are assigned to in-plane deformation modes of the ligand. For \([W(CO)_4(Me-DAB)]\) these deformation vibrations are not correctly calculated. Similar results were obtained for the calculations for other Me–DAB model complexes. The band found at 623 cm\(^{-1}\) (calculated at 616 cm\(^{-1}\)) is due to a \(\delta(WCO)\) mode, while the ones observed at 480 and 431 cm\(^{-1}\) (calculated at 449 and 427 cm\(^{-1}\), respectively) belong to combined \(v_5(WC)\) and
\(\nu_s(\text{WN})\) modes. Additionally, the band at 222 cm\(^{-1}\) has been attributed to \(\nu_s(\text{WN})\) on the basis of isotope labelling studies,\(^{38}\) and is calculated at 227 cm\(^{-1}\). The occurrence of these extra rR bands is caused by the increase of interaction between the metal \(d_e\) and ligand \(\pi^*\) orbitals in both the HOMO and LUMO going from the Re to the W complex, leading to delocalization of these orbitals. As a result the electronic transition has less charge transfer character and obtains partial metal–ligand bonding to anti-bonding character. As such a transition causes a weakening of the metal–nitrogen bonds and distortion of the iPr-DAB ligand, it invokes rR effects for deformation modes of iPr-DAB and for \(\nu_s(W-N)\).\(^{37}\) This \(d_e-\pi^*\) interaction can be further enhanced by increasing the metal \(d\)-orbital energy (e.g. in [Ni(CO)\(_2\)(tBu–DAB)]),\(^{39}\) or by decreasing the \(\pi^*(\alpha\text{-diimine})\) orbital energy (e.g. in [W(CO)\(_4\)(R–DAB)] (R = pTol, Mes)).\(^{37}\) The rR spectra of these complexes show much higher intensities for the ligand deformation modes below 1000 cm\(^{-1}\) while at the same time both \(\nu_s(\text{CO})\) and \(\nu_s(\text{CN})\) have become much weaker. In extreme cases, \(\nu_s(\text{CO})\) and \(\nu_s(\text{CN})\) virtually disappear.

So far, the co-ligands were not directly involved in the HOMO→LUMO transition. However, this situation changes if a co-ligand is introduced with high-lying filled orbitals which contribute to the HOMO. For instance, in the case of the halide (X) complexes [Re(X)(CO)\(_3\)(\(\alpha\text{-diimine})\)] a \(p_n(\text{X})\) orbital contributes to the HOMO, causing a change of character of the low-energy transition from Metal-to-Ligand Charge Transfer into Halide-to-Ligand Charge Transfer going from X = Cl\(^-\) to X = I\(^-\).\(^{12}\) Another ligand with a high-lying orbital is the methyl ligand. The influence of the introduction of this ligand in \(d^6\) metal–diimine complexes on the rR spectra is discussed in the next section.

(3) The influence of methyl ligands

[Re(CH\(_3\))(CO)\(_3\)(iPr–DAB)].\(^{40}\) Due to the electron donating character of the methyl group, the lowest-energy MLCT transition is shifted to longer wavelength with respect to that of [Re(PPh\(_3\))(CO)\(_3\)(iPr–DAB)]\(^+\). Although, UV-photoelectron spectroscopic studies showed that the \(\sigma(\text{Re–CH}_3)\) orbital itself lies at only slightly lower energy than the metal \(d\)-orbitals,\(^{40}\) the rR spectra show only a small influence of the CH\(_3\) group. Thus, similarly to [Re(PPh\(_3\))(CO)\(_3\)(iPr–DAB)]\(^+\), \(\nu_s(\text{CO})\) (at 1988 cm\(^{-1}\)) and \(\nu_s(\text{CN})\) (at 1511 cm\(^{-1}\)) are observed. The shifts of these vibrations to lower frequency compared to the PPh\(_3\) complex are again in correspondence with the higher electron density on the metal, leading to an increase of both metal→\(\text{CO}\) and metal→\(\alpha\text{-diimine}\) \(\pi\)-backbonding. A weak band at 1156 cm\(^{-1}\) is the first evidence that the CH\(_3\) ligand participates in the electronic transition. Since for the
corresponding complexes \([\text{Re}(R)(\text{CO})_3(\text{dmb})]\) (\(R = \text{CH}_3, \text{CD}_3; \text{dmb} = \text{4},\text{4}'-\text{dimethyl-2,2'-bipyridine})\) this vibration was found to shift from 1166 to 898 cm\(^{-1}\) going from the \(\text{CH}_3\) to the \(\text{CD}_3\) complex,\(^{16}\) it is assigned to the symmetrical \(\text{CH}_3\) deformation vibration, \(\delta(\text{CH}_3)\). A similar vibration was found for \([\text{Re}(\text{CH}_3)(\text{CO})_3]\).\(^{41}\) The weak band at 732 cm\(^{-1}\) is assigned to the corresponding rocking mode of the \(\text{CH}_3\) group, \(\rho(\text{CH}_3)\). Further bands are observed at 503, 488 and 451 cm\(^{-1}\), all of which are very weak and belong to metal–ligand stretching and deformation modes, probably similar to the ones found for \([\text{W}(\text{CO})_4(\text{iPr-DAB})]\). In conclusion, the rR spectra of \([\text{Re}(\text{CH}_3)(\text{CO})_3(\text{iPr-DAB})]\) are very similar to those of \([\text{Re}(\text{PPh}_3)(\text{CO})_3(\text{iPr-DAB})]^{+}\), and the methyl ligand of the former complex is only weakly involved in the charge transfer transition.

\[\text{[Ru(Cl)(R)(CO)_2(iPr-DAB)] \quad (R = \text{CH}_3, \text{CD}_3).}^{13}\] RR spectra were recorded for the complexes \([\text{Ru(Cl)(R)(CO)_2(iPr-DAB)] \quad (R = \text{CH}_3, \text{CD}_3}\) (Figure 8.4) and DFT vibrational calculations were performed on the model complexes \([\text{Ru(Cl)(R)(CO)_2(Me-DAB)] \quad (R = \text{CH}_3, \text{CD}_3}\). The rR spectra of \([\text{Ru(Cl)(R)(CO)_2(iPr-DAB)] \quad (R = \text{CH}_3, \text{CD}_3}\) are very similar to
those of the Re–methyl complex discussed above. Thus, $v_s$(CO) is observed at 2016 cm$^{-1}$ (calculated at 2110 cm$^{-1}$ for the model complex). Furthermore, $v_s$(CN) is observed at 1573 cm$^{-1}$ (calculated at 1626 cm$^{-1}$). In addition, a weak band is observed at 1209 cm$^{-1}$ (calculated at 1269 cm$^{-1}$) which shifts to 924 cm$^{-1}$ (calculated at 962 cm$^{-1}$) on deuteration of the methyl group. Again this band is attributed to $\delta$(CH$_3$/CD$_3$). A strongly enhanced band is observed at ca. 490 cm$^{-1}$ for both the CH$_3$ and CD$_3$ complex. For the [Ru(l)(R)(CO)$_2$(iPr–DAB)] complexes, this band was assigned to $v_s$(Ru–CO) and not to $v$(Ru–CH$_3$), in view of the lack of shift on deuteration.\textsuperscript{15} The present calculations show that this normal mode (calculated at 500 cm$^{-1}$, observed at 492 cm$^{-1}$) has $v_s$(Ru–N) and $v_s$(Ru–CO) character with a $v$(Ru–CH$_3$) contribution for the CH$_3$ complex. According to the calculations, $v$(Ru–CD$_3$) does not contribute to this normal mode (calculated at 496 cm$^{-1}$, observed at 490 cm$^{-1}$) in the CD$_3$ complex.

$$[\text{Ru(SnPh}_3\text{)(R)(CO)}_2\text{(iPr–DAB)]. (R = \text{CH}_3, \text{CD}_3).$$\textsuperscript{19} Replacement of Cl$^-$ by an SnPh$_3$ ligand drastically changes the electronic structure of these complexes. The methyl and SnPh$_3$ ligands are in axial positions and the HOMO consists of the antisymmetric combination of their lone pairs with a small contribution of a p(Ru) orbital.\textsuperscript{14} This $\sigma$(Sn–Ru–Me) orbital has the same symmetry as the $\pi^*$ (iPr–DAB) orbital. The main difference with the preceding complexes is that instead of $d_\pi$(Ru), $\sigma$(Sn–Ru–Me) is responsible for the $\pi$-backbonding to iPr–DAB in the HOMO and that the charge transfer transition to this ligand originates from this orbital. This transition is called a $\sigma\rightarrow\pi^*$ or Sigma-Bond-to-Ligand Charge Transfer (SBLCT) transition. As is shown hereinafter, the rR spectra of these and other metal–methyl complexes with a lowest SBLCT state are different from those discussed before. For the assignment of the rR bands of this complex (Figure 8.4), the DFT calculated vibrations of the model complex [Ru(CH$_3$)(SnMe$_3$)(CO)$_2$(Me–DAB)] are used.

The first striking observation is the absence of an rR effect for $v_s$(CO), which implies that the electron density on the central metal atom is hardly affected by the SBLCT transition. This may be due to the fact that the central metal atom is hardly involved in this transition, or because the transition has little charge transfer character due to a strong $\sigma$–$\pi^*$ interaction, comparable with the $d_\pi$–$\pi^*$ interaction in the complexes [Ni(CO)$_2$(tBu–DAB)] and [W(CO)$_4$(R–DAB)] (R = pTol, Mes) (\textit{vide supra}). Probably, both effects are of importance here. The DFT calculations show that the p(Ru) orbital contributes merely ca. 12% to the HOMO and LUMO of the model complex [Ru(SnH$_3$)(CH$_3$)(CO)$_2$(H–DAB)].\textsuperscript{14} On the other hand, the small solvatochromic shift of the SBLCT transition\textsuperscript{19} points to a strong $\sigma$–$\pi^*$
interaction in ground and excited states. The low frequency of $\nu_s$(CN) (observed at 1491 cm$^{-1}$, calculated at 1543 cm$^{-1}$) is due to a strong $\pi$-backbonding to iPr-DAB. At 1156 cm$^{-1}$, $\delta$(CH$_3$) is found, shifting to 884 cm$^{-1}$ on deuteration. This vibration is strongly resonance enhanced for this complex since the SBLCT transition lowers the electron density in the $\sigma$(SnPh$_3$–Ru–CH$_3$) orbital, causing a change of the methyl bonds and angles and accordingly a rR effect for $\delta$(CH$_3$). In the case of [Ru(Cl)(CH$_3$)CO)$_2$(iPr-DAB)] the rR effect of $\delta$(CH$_3$) is weaker, since the methyl ligand of this complex has only a minor contribution to the HOMO and the lowest MLCT transition. The low frequency of $\nu_s$(CN) and the appearance of $\delta$(DAB) deformation vibrations at 950 and 836 cm$^{-1}$ point again to a strong delocalization of HOMO and LUMO, just as in the case of [W(CO)$_4$(iPr–DAB)] (vide supra). In addition, however, a new (weak) band shows up at 1296 cm$^{-1}$. According to the calculations, it mainly consists of a symmetric in-plane movement of the imine hydrogen atoms, coupled to a symmetric CN stretching vibration, and is therefore denoted as $\delta$(CH), like in the case of [W(CO)$_4$(iPr–DAB)].

![Figure 8.5](image)

Figure 8.5 Pictorial representation of the $\delta$(CH) vibration.

Figure 8.5 shows a pictorial representation of this vibration. It was shown in the case of [W(CO)$_4$(iPr–DAB)] (vide supra) that the large difference between the observed (1296 cm$^{-1}$) and the calculated value (1407 cm$^{-1}$) is due to the sensitivity of the frequency of this vibration to the nature of R in the R–DAB ligand. Further bands are observed at 610 and 241 cm$^{-1}$ (calculated 618 and 239 cm$^{-1}$) belonging to $\delta$(RuCO) and $\nu_s$(RuN), respectively, according to the calculations.
[Pt(R)₄(iPr-DAB)] (R = CH₃, CD₃). The two axial methyl groups of this complex contribute to two \( \sigma(CH₃-M-CH₃) \) orbitals. One of these is the HOMO which consists of the antisymmetric combination of the axial methyl \( sp^3 \) orbitals, of \( \pi^*(iPr-DAB) \) and a minor contribution from a \( d(Pt) \) orbital. The rR spectra, obtained by excitation into the SBLCT transition of [Pt(R)₄(iPr-DAB)] (R = CH₃, CD₃) (Figure 8.4) are interpreted with the help of DFT calculations on the [Pt(R)₄(Me-DAB)] (R = CH₃, CD₃) model complexes.

Two major bands are found in the rR spectra. First of all, \( \nu_s(CN) \) is observed at ca. 1565 cm\(^{-1}\) (calc. at ca. 1595 cm\(^{-1}\)) for both the CH₃ and CD₃ complexes (Table 8.1). However, the most intense rR band is found at 1175 cm\(^{-1}\) for the CH₃ complex and at 894 cm\(^{-1}\) for the CD₃ complex. This band is again assigned to the symmetrical deformation of the methyl groups, \( \delta(CH₃/CD₃) \), on the basis of the shift on deuteration and the calculated frequencies of 1213 and 923 cm\(^{-1}\) for the CH₃ and CD₃ model complexes, respectively. The rR intensity of \( \delta(CH₃/CD₃) \) is much higher for these complexes than for [Re(CH₃)(CO)₃(iPr-DAB)] and [Ru(Cl)(R)(CO)₂(iPr-DAB)] (R = CH₃, CD₃) and even higher than for [Ru(CH₃)(SnPh₃)(CO)₂(iPr-DAB)]. This agrees with the results from DFT calculations that in the [Pt(R)₄(iPr-DAB)] (R = CH₃, CD₃) complexes the \( \sigma(CH₃) \) orbitals are the main contributors to the HOMO from which the SBLCT transition originates. For [Pt(CH₃)₄(iPr-DAB)], \( \nu_s(PtC)_{eq} \) and \( \nu_s(PtC)_{as} \) are found as very weak bands at 517 and 469 cm\(^{-1}\), respectively. Although especially the latter vibration can be expected to be vibronically coupled to the SBLCT electronic transition, the absence of strong resonance enhancement contradicts this expectation.

(4) The influence of metal–metal bonds

Just as the methyl ligand, a metal fragment bonded to the central metal atom can affect the rR spectra in various ways, depending on the involvement of the metal–metal bonding orbital in the excited electronic transition. If in the complex [Ru(Cl)(Me)(CO)₂(iPr-DAB)] the methyl ligand is replaced by SnPh₃, the rR spectrum of the resulting complex [Ru(Cl)(SnPh₃)(CO)₂(iPr-DAB)] is even simpler than that of [Ru(Cl)(Me)(CO)₂(iPr-DAB)]. In this case only the Raman band belonging to \( \nu_s(CN) \) is resonance enhanced. It has shifted from 1576 to 1543 cm\(^{-1}\), pointing to an increase of \( \pi \)-backbonding on going to [Ru(Cl)(SnPh₃)(CO)₂(iPr-DAB)]\(^{14,19}\). The rR band belonging to \( \nu_s(CO) \) has disappeared. This could imply a loss of charge transfer character, but the relatively high frequency of \( \nu_s(CN) \) (1543 cm\(^{-1}\)) points to a weak metal-diimine \( \pi \)-backbonding and an appreciable transfer of
Chapter 8. Influences on the Resonance Raman Spectra of $d^6$ Metal-Diimine Complexes

charge during the transition. Hence, the disappearance of $\nu_s$(CO) is probably at least in part due to the fact that the transition has partly XLCT ($X = Cl$) character, in line with similar observations when Cl$^-$ is replaced by I$^-$ in $[\text{Ru(Cl)(CH}_3)(\text{CO})_2(iPr-DAB)]$.$^{13}$ In addition, only very weak bands are observed at 605, 478 and 244 cm$^{-1}$, due to $\delta$(RuCO), $\nu_s$(Ru–C) and $\nu_s$(Ru–N) respectively, in accordance with the assignments of bands at similar frequencies for e.g. $[\text{W(CO)}_4(iPr-DAB)]$ (vide supra).

The influence of replacing a methyl group by a metal fragment is much larger when the methyl ligand in $[\text{Re(CH}_3)(\text{CO})_3(iPr-DAB)]$ is substituted by a Re(CO)$_5$ fragment. The HOMO of $[\text{Re(Re(CO)}_5)(\text{CO})_3(iPr-DAB)]$ was shown to be the $\sigma$(Re–Re) orbital,$^{13}$ but the lowest-energy allowed transition has $d_x$(Re)$\rightarrow$$\pi^*$(iPr-DAB) (MLCT) character.$^{11}$ Again, the absence of any $\nu$(CO) band in the rR spectrum obtained by excitation into this MLCT transition, shows the small degree of charge transfer character, due to the fact that both HOMO and LUMO are delocalized over the Re–DAB metallacycle. In this case the delocalization is so extensive that even $\nu_s$(CN) (observed at 1467 cm$^{-1}$) has become weak. In fact the strongest bands in the rR spectrum are now the $\delta_s$(DAB) bands at 957 and 838 cm$^{-1}$. The band observed at 1289 cm$^{-1}$ is attributed to the same $\delta_s$(CH) vibration that is observed for $[\text{Ru(R(SnPh}_3)(\text{CO})_2(iPr-DAB)] (R = CH}_3$, CD$_3$) (vide supra).

The last part of this section is devoted to trinuclear metal–metal bonded complexes. In these complexes the metal fragments participate in the HOMO and in the lowest-energy transition, which therefore has SBLCT character, just as in the case of $[\text{Pt(CH}_3)_4(iPr-DAB)]$ (vide supra).

$[\text{Pt(SnPh}_3)_2(CH}_3)_2(iPr-DAB)]$.$^{21}$ In this complex, $\pi$-backbonding lowers the frequency of $\nu_s$(CN) to the very low value of 1474 cm$^{-1}$. This is accompanied by an intensity increase of $\delta_s$(CH) at 1292 cm$^{-1}$ (Figure 8.6) Apparently, a frequency lowering of $\nu_s$(CN) causes a coupling of this vibration to $\delta_s$(CH), which coupling results in resonance enhancement of the latter vibration. This change in enhancement of $\delta_s$(CH) appears to be rather sudden, since this vibration is only weak for $[\text{Ru(CH}_3)(\text{SnPh}_3)(\text{CO})_2(iPr-DAB)]$ ($\nu_s$(CN) at 1492 cm$^{-1}$), but strongly enhanced for $[\text{Pt(SnPh}_3)_2(CH}_3)_2(iPr-DAB)]$ ($\nu_s$(CN) at 1474 cm$^{-1}$). However, the $\delta_s$(DAB) vibrations (observed at 949 and 834 cm$^{-1}$) are only very weakly enhanced. This means that in spite of the strong $\pi$-backbonding in this complex, its SBLCT transition does not cause a distortion of the Pt–iPr–DAB metallacycle, which indicates that the delocalization of HOMO and LUMO is rather weak and SBLCT transition
in this complex has appreciable charge transfer character. With decreasing charge transfer character, the DAB deformation modes become enhanced (vide infra).

![Raman Spectra](image)

**Figure 8.6** RR spectra of (a) [Pt(SnPh$_3$)$_2$(CH$_3$)$_2$(iPr–DAB)] ($\lambda_{exc} = 595.6$ nm, recorded at 90 K), (b) [Ru(SnPh$_3$)$_2$(CO)$_2$(iPr–DAB)] ($\lambda_{exc} = 457.9$ nm) and (c) [Ru{RuCp(CO)$_2$}(CO)$_2$(iPr–DAB)] ($\lambda_{exc} = 590.0$ nm) in KNO$_3$. Asterisks denote NO$_3^-$ bands.

$[M$(SnPh$_3$)$_2$(CO)$_2$(iPr–DAB)] (M = Ru, Os).$ In order to investigate the influence of the central metal atom on the electronic structure and SBLCT transition, the rR spectra of both the Ru and Os complexes were studied. The spectrum of $[Ru$(SnPh$_3$)$_2$(CO)$_2$(iPr–DAB)] is shown in Figure 8.6. In addition, DFT calculations were performed on the model complexes $[Ru$(SnH$_3$)$_2$(CO)$_2$(iPr–DAB)], $[Ru$(SnH$_3$)$_2$(CO)$_2$(Me–DAB)] and $[Os$(SnH$_3$)$_2$(CO)$_2$(Me–DAB)] in order to deduce the influence of both the central metal atom and the substituents R of R–DAB on the vibrational frequencies.

The observed $v_5$(CN) and $\delta$(CH) bands in the rR spectra, obtained by excitation into the SBLCT transition of the $[M$(SnPh$_3$)$_2$(CO)$_2$(iPr–DAB)] (M = Ru, Os) complexes, are hardly shifted compared to those of $[Pt$(SnPh$_3$)$_2$(CH)$_2$(iPr–DAB)]. Thus, $v_5$(CN) is observed at ca. 1473 cm$^{-1}$ and $\delta$(CH) at 1292 and 1278 cm$^{-1}$ for M = Ru and Os, respectively. The
DFT calculations show that the frequency of $\Delta^r_{\text{CH}}$ is very sensitive to the substituent R of the R-DAB ligand, since the calculated frequency of $\Delta^r_{\text{CH}}$ of $[\text{Ru(SnH}_3)_2\text{(CO)}_2\text{(R-DAB)}]$ (R = Me, iPr) shifts from 1405 cm$^{-1}$ to 1326 cm$^{-1}$ going from R = Me to R = iPr. As expected, the latter value is a few percent too high, compared to the observed frequency (1292 cm$^{-1}$). The lowest-energy absorption bands of $[\text{M(SnPh}_3)_2\text{(CO)}_2\text{(iPr-DAB)}]$ (M = Ru, Os) are less solvatochromic ($\Delta = \nu(\text{MeCN}) - \nu(\text{toluene}) = 500 - 600$ cm$^{-1}$) than that of $[\text{Pt(SnPh}_3)_2(\text{CH}_3)_2\text{(iPr-DAB)}]$ ($\Delta = 900$ cm$^{-1}$). This explains the high intensity of the $\Delta^r_{\text{DAB}}$ vibrations in the rR spectra of $[\text{M(SnPh}_3)_2\text{(CO)}_2\text{(iPr-DAB)}]$ (M = Ru, Os) and their absence in the spectrum of $[\text{Pt(SnPh}_3)_2(\text{CH}_3)_2\text{(iPr-DAB)}]$ (vide supra), since these vibrations become enhanced whenever the HOMO and LUMO orbitals become strongly delocalized. Interestingly, the observed frequencies of all bands hardly shift going from the Ru to the Os complex, which supports the results of our DFT calculations that Ru and Os orbitals are only minor contributors to the HOMO and LUMO. It also implies that the $\pi$-backbonding to iPr-DAB, reflected in a low frequency of $\nu_6$(CN), can only be caused by a strong $\sigma$-$\pi^*$ interaction between the SnPh$_3$ ligands and iPr-DAB. The strong $\sigma$-$\pi^*$ interaction is also evident from a large $J_{\text{Sn-H}}$ coupling constant for the imine protons of iPr-DAB.$^{19,22}$ Furthermore, the crystal structure of this complex shows a significantly elongated CN bond.$^{44}$

Similar low-frequency bands are observed for these complexes as for other complexes with a delocalized electronic system. Thus $\Delta^r_{\text{MCO}}$ is observed at 610 cm$^{-1}$, $\nu_4$(MC) at 419 cm$^{-1}$ and $\nu_4$(MN) at ca. 249 cm$^{-1}$. Although the intensities of these bands are lower than those of the other ones, the distortion along these normal modes is significant in view of their low frequencies.

$[\text{Ru[RuCp(CO)]_2(CO)}_2\text{(iPr-DAB)}]$.$^{23}$ This complex is an example of an extremely delocalized electronic system, shown by e.g. the solvatochromism of its first absorption band, which is negligible. Just as in the case of $[\text{Re[Re(CO)]_5(CO)}_3\text{(iPr-DAB)}]$ this leads to a complete disappearance of $\nu_4$(CN) and $\Delta^r(\text{CH})$, while the $\Delta^r_{\text{DAB}}$ bands and the metal–ligand and metal–metal stretching modes are the strongest in the rR spectrum (Figure 8.6). This implies that the SBLCT transition of this complex has metal–ligand and metal–metal bonding to antibonding character, which is accompanied by a distortion of the iPr-DAB ligand.
8.5 Conclusions

The preceding section gave an overview of the rR spectra of a number d^6 metal-diimine complexes, with special attention paid to three factors that influence the appearance of these spectra. These three factors are: (1) the π-backbonding to the iPr-DAB ligand, (2) the delocalization of the frontier orbitals determining the degree of charge transfer character of the excited transition and (3) the character of that transition.

Whenever a strong π-backbonding is present in the ground state of the complex, whether by dπ−π* or σ−π* interaction, the symmetric CN stretching vibration is lowered in frequency. If ν_s(CN) is shifted to a frequency lower than ca. 1490 cm^{-1}, a concomitant resonance enhancement of δ_s(CH) (Figure 8.5) is observed. Apparently, this is due to δ_s(CH) obtaining some ν_s(CN) character, thus being vibrationally coupled to the electronic transition.

Delocalization of the orbitals between which the electronic transition occurs, results in the loss of charge transfer character. As a consequence, stretching vibrations, such as ν_s(CO) and in extreme cases also ν_s(CN) disappear from the rR spectrum, while δ_s(DAB) vibrations gain intensity. Since δ_s(CH) is coupled to ν_s(CN), the bands due to both vibrations decrease simultaneously in intensity when delocalization increases.

In the case of methyl complexes, the change in character of the electronic transition from MLCT to SBLCT gives rise to strong resonance enhancement of intensity for the symmetric methyl group deformation vibration. Remarkably the metal–carbon stretching vibration is not resonantly enhanced. Hence, the metal–methyl ligand stretching vibration is generally not a good indicator of electronic transition character, in contrast to δ_s(CH3).

One of the remarkable results of this study is that, while the rR spectra of e.g. [Ru(Cl)(CH3)(CO)2(iPr−DAB)] and [Ru(SnPh3)2(CO)2(iPr−DAB)] are very different in appearance, most of these differences can be rationalized in terms of π-backbonding and orbital delocalization rather than attributed to a change in the character of the electronic transition.

A large part of the assignments of the vibrations were based on DFT-calculations. As such they have proven very useful. However, it was also shown that structural simplifications in the calculated complex (e.g. iPr−DAB to Me−DAB) may have profound influence on the frequency and character of certain calculated vibrations.
8.6 References

Chapter 8. Influences on the Resonance Raman Spectra of \(d^6\) Metal–Diimine Complexes


This thesis deals with the electronic transitions and excited state properties of a number of d⁶ 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(SnPh₃)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 ν₄(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$_3$)(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-dimine 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\textsubscript{3})(CO)\textsubscript{2}(iPr-DAB)] (M = Ru, Os) (chapter 3) for Pt (chapter 7) red-shifted absorption and emission energies of the resulting [Pt(SnPh\textsubscript{3})(Me)\textsubscript{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\textsubscript{3})(CO)\textsubscript{2}(pAn-BIAN)] (chapter 3) and $\lambda_{em} = 855$ nm for [Ru{RuCp(CO)\textsubscript{2}}\textsubscript{2}(CO)\textsubscript{2}(iPr-DAB)] (chapter 4). Interestingly, the use of the electron donating RuCp(CO)\textsubscript{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 $\sigma$–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 *ab initio* calculations on the ground and excited states of the model complex [Ru(SnH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{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\textsubscript{3})\textsubscript{4}(iPr-DAB)] and [Ru(R)(SnPh\textsubscript{3})(CO)\textsubscript{2}(iPr-DAB)] ($R = \text{CH}_3, \text{CD}_3$). 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 SBLC T state. For the iPr-complex homolysis is observed at longer wavelength irradiation than for the methyl derivative, indicating that in the former case the SBLC T-state is lower in energy.

It is clear from the foregoing that much more is known now about SBLC T states and transitions in d⁶ metal-diimin e complexes than when this PhD project started. The remaining question is along which lines research of SBLC T 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 SBLC T 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 SBLC T 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 SBLC T-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.
SAMENVATTING

Dit proefschrift beschrijft het onderzoek naar de eigenschappen van de electronische overgangen en aangeslagen toestanden van een reeks $d^6$ metaal–metaal en metaal–alkyl gebonden organo-overgangsmetaalcomplexen. In het inleidende hoofdstuk 1 werden de belangrijkste wetenschappelijke doelen van dit promotieonderzoek uiteengezet, alsmede de methoden om deze te bereiken. Het uitzonderlijk fotochemisch en fotofysisch gedrag van deze complexen is het gevolg van het feit dat hun laagst-energetische electronenovergang gepaard gaat met ladingsoverdracht vanuit een sigma-bindende baan naar een ligandorbitaal. In dit proefschrift wordt hiervoor de afkorting gebruikt van de Engelse term, SBLCT. Zoals beschreven in paragraaf 1.3, heeft dit twee belangrijke gevolgen voor de eigenschappen van de aangeslagen toestand. Aan de ene kant leidt verlies aan elektronendichtheid tot verzwakking van de σ-binding. Dit veroorzaakt fotochemische bindingshomolyse, die zeer efficiënt kan zijn. Aan de andere kant heeft de SBLCT-toestand een extreem lange levensduur, zolang bindingshomolyse niet efficiënt is. Een dergelijke reactie kan inefficiënt zijn vanwege sterke metaal–ligand bindingen of omdat de temperatuur te laag is om thermisch geactiveerde chemische reacties uit de aangeslagen toestand toe te staan.

Het eerste doel van dit promotieonderzoek was om experimenteel bewijs te verkrijgen voor het SBLCT-karakter van laagliggende toegestane electronische overgangen. De gekozen experimentele methode was Resonantie Raman (rR) spectroscopie. Uit rR-spectra kan afgeleid worden welke trillingen worden beïnvloed door bepaalde electronische overgangen en hieruit kan informatie verkregen worden over het karakter van deze overgangen. Zo zijn bijvoorbeeld de rR-spectra, verkregen in hoofdstuk 3 door excitatie in respectievelijk de MLCT-overgang van $[\text{Ru(Cl)(Me)(CO)}_2(\text{iPr–DAB})]$ en de SBLCT-overgang van $[\text{M(SnPh}_3)_2(\text{CO})_2(\text{iPr–DAB})]$, totaal verschillend. Het spectrum van de eerste verbinding laat zien dat de symmetrische CO- en CN-strektrilling evenals de Ru–CO-deformatietrilling worden beïnvloed door de MLCT-overgang. In het spectrum van het tweede complex is $v_s$(CO) afwezig, maar zijn vele in-het-vlak en uit-het-vlak deformatietrillingen aanwezig. Deze trillingen werden deels door middel van vibratieberekeningen op DFT-niveau toegekend. Echter, zoals hoofdstuk 8 laat zien, kunnen deze verschillen alle eerder verklaard worden met een toename van metaal–ligandinteractie gaande van het eerste naar het tweede type complexen dan met een verschil in karakter van de electronische overgang. Daarom is
Samenvatting

rR-spectroscopie voor deze complexen geen geschikt middel om het karakter van de electronische overgang te bepalen. Aan de andere kant, bleek rR-spectroscopie wel uitermate geschikt te zijn om het SBLCT-karakter van de electronische overgangen van metaal–methylgebonden complexen vast te stellen (hoofdstukken 7 en 8). Hiertoe werd de Raman band van de symmetrische methyl-deformatietrilling gebruikt. In rR-spectra, verkregen door excitatie in de MLCT-overgang van bijvoorbeeld [Ru(Cl)(Me)(CO)₂(iPr-DAB)] of [Re(Me)(CO)₃(iPr-DAB)] was deze band nauwelijks te onderscheiden, terwijl het de sterkste band was in het rR-spectrum van [Pt(Me)₄(iPr-DAB)], waarvan de electronische overgang SBLCT-karakter heeft. De conclusie van de resultaten beschreven in hoofdstuk 8 is dat rR-spectroscopie een uitstekende techniek kan zijn om experimenteel bewijs te verkrijgen voor het karakter van een electronische overgang, maar zeker niet voor alle systemen.

Een tweede vraag was of complexen met een laagst 3SBLCT-toestand fotostabiel gemaakt kunnen worden. Het meest fotostabiele d⁸-overgangsmetaalcomplex dat tot nu toe bekend was, is [Re(SnPh₃)(CO)₃(dmb)], hoewel dat complex nog steeds fotochemisch ontleedt met een kwantumopbrengst bij kamertemperatuur van 0.03–0.06 afhankelijk van de excitatiegolflengte. Van de in dit proefschrift beschreven complexen, bleken [Ru(SnPh₃)₂(CO)₂(pAn-DAB)], [Ru(SnPh₃)₂(CO)₂(pAn-BIAN)], [Os(SnPh₃)₂(CO)₂(iPr-DAB)] en [Os(SnPh₃)₂(CO)₂(dmb)] alle significant fotostabiel (hoofdstuk 3). Voor de Ru-complexen is dit het gevolg van verlaging van de energie van de SBLCT toestand, aangezien het gebruikte α-diimine ligand een zeer laagliggende π*-orbitaal heeft. Dit verhoogt de energiebarrière voor de thermisch geactiveerde reactie uit de gerelaxeerde aangeslagen toestand. Voor de Os-complexen is het de inherent sterke Os–Sn binding, die de efficiëntie van de fotochemische homolysereactie verlaagt. Een belangrijk gevolg van de afname van de fotolabiliteit was dat de levensduur van de aangeslagen bij kamertemperatuur aanzienlijk verlengd werd (tot 3.6 µs in het geval van [Ru(SnPh₃)₂(CO)₂(pAn-BIAN)]). De lage energie van de aangeslagen toestand van de Ru-complexen is een extra voordeel in het kader van mogelijke toepassing als nabij-infrarood emitterende labels (hoofdstuk 3).

Hoewel deze resultaten al aangeven dat SBLCT-toestanden, ondanks hun reactiviteit, veel langer kunnen leven dan MLCT-toestanden, bleek dit verschil veel uitgesprokener te zijn in lage-temperatuur glazen, waar homolysereacties de levensduur van de aangeslagen toestand niet beperken. Voornamelijk door een veel kleinere vervorming in de aangeslagen toestand, hetgeen leidt tot een verminderde vibrationele overlap tussen grond- en aangeslagen toestand, bleken SBLCT-toestanden veel langer te leven dan MLCT-toestanden van vergelijkbare complexen. De langste levensduur van de aangeslagen toestand van 1.1 ms werd verkregen.
voor [Ru(SnPh₃)₂(CO)₂(dmb)] in 2-MeTHF bij 90 K (hoofdstuk 3).

Het is interessant dat vervanging van Ru door Os in [Ru(SnPh₃)₂(CO)₂(dmb)] leidde tot een vijfvoudige afname van de levensduur van de aangeslagen toestand, terwijl de absorptie- en emissie-energie onveranderd bleven. Op deze wijze kan de invloed van spin-baankoppeling op de levensduur bestudeerd worden onafhankelijk van de vervorming van het complex in de aangeslagen toestand en de energie van die toestand. Vervanging van Ru en Os in [M(SnPh₃)₂(CO)₂(iPr-DAB)] (M = Ru, Os) (hoofdstuk 3) door Pt (hoofdstuk 7) leidde tot roodverschuiving van de absorptie- en emissie-energie van het gevormde [Pt(SnPh₃)₂(Me)₂(iPr-DAB)] complex, ten gevolge van de afname van delocalisatie in de grensorbitalen, hetgeen de overlapstabilisatie en dus de HOMO–LUMO afstand verkleint.

Hoofdstukken 3 en 4 beschrijven de pogingen om de absorptie- en emissie-energie naar het rode of nabij-infrarode (NIR) gebied van het spectrum te verschuiven. De benadering gebruikt in hoofdstuk 3 was om de energie van de LUMO te verlagen, terwijl in hoofdstuk 4 de energie van de HOMO verhoogd werd. Beide benaderingen resulteerden in NIR-emitterende verbindingen, bijvoorbeeld λ_em = 821 nm voor [Ru(SnPh₃)₂(CO)₂(pAn–BIAN)] (hoofdstuk 3) en λ_em = 855 nm voor [Ru{RuCp(CO)₂}₂(CO)₂(iPr–DAB)] (hoofdstuk 4). Het is opmerkelijk dat het gebruik van electron-donerende liganden in het laatste complex bovendien het één-electron-geoxideerde product stabiliseert, hetgeen dit complex tot de enige vertegenwoordiger van deze reeks complexen maakt waarvoor zo'n geoxideerd deeltje ooit is waargenomen. Echter heeft de benadering waarbij de energie van de σ-orbitaal wordt verhoogd als nadeel dat de resulterende complexen bij kamertemperatuur zeer fotolabeliel zijn. Hoewel NIR-emitterende complexen werden verkregen door middel van beide benaderingen, hebben al deze gegevens betrekking op metingen aan de verbindingen opgelost in vaste glazen bij lage temperatuur. Bij kamertemperatuur werd geen emissie voor deze complexen waargenomen, terwijl de emissie bij lage temperatuur en die van vergelijkbare complexen die bij hogere energie emitteren, nogal zwak is. De reden voor de lage emissiekwantumopbrengst is nog niet duidelijk, maar gezien de resultaten van recente ab initio berekeningen aan de grond- en aangeslagen toestanden van [Ru(SnH₃)₂(CO)₂(Me–DAB)] wordt voorgesteld, dat de intersystem crossing van de optisch bezette ¹SBLCT-toestand naar de emitterende ³SBLCT-toestand inefficiënt is, ten gevolge van het grote energieverschil tussen deze twee toestanden en vanwege concurrerend niet-stralend verval naar een andere (niet-emitterende) triplet aangeslagen toestand (met ³MLCT-karakter). Dit maakt toekomstige toepassing van zulke complexen als luminofoeren tamelijk onwaarschijnlijk.
De andere hoofdeigenschap van SBLCT-toestanden, hun efficiënte radicaalvorming, is succesvol in de praktijk gebruikt aangezien verscheidene $d^6$ metaal–alkylcomplexen goede foto-initiatoren voor radicaalpolymerisaties bleken te zijn. **Hoofdstuk 5** rapporteert over een meer fundamenteel onderzoek van deze radicalen, namelijk een FT-EPR studie van de methylradicalen, die verkregen werden door bestraling van oplossingen van $[\text{Pt}(\text{CH}_3)_4(\text{iPr-DAB})]$ en $[\text{Ru}(\text{R})(\text{SnPh}_3)(\text{CO})_2(\text{iPr-DAB})]$ ($\text{R} = \text{CH}_3, \text{CD}_3$). De resultaten van dit onderzoek bevestigen het triplet karakter van de aangeslagen toestand waaruit de radicalen worden gevormd. Door uitgebreide variatie van het oplosmiddel werd aangetoond dat de chemisch-geïnduceerde dynamische electronegative polarisatie (CIDEp) zijn oorsprong heeft in gecombineerde bijdragen van de ST$_x$-en ST$_{-1}$-radicaalpaarmechanismen. De afwezigheid van door het triplet-mechanisme geïnduceerde CIDEp in de radicalen, die zijn ontstaan door in te stralen in de laagst-energetische absorptieband, suggereert dat de radicaalvorming een zeer snel proces is. Zeer interessant is het feit dat het CIDEp-patroon van de fotochemisch gegenereerde radicalen sterk afhangt van de excitatiegolflengte. Deze zeldzame waarneming bewijst dat de radicaalvorming via verschillende paden verloopt afhankelijk van de excitatiegolflengte.

**Hoofdstuk 6** beschrijft twee nieuwe complexen, cis-[$\text{Rh}(\text{R})_2(\text{I})(\text{CO})(\text{dmb})]$ ($\text{R} = \text{Me}, \text{iPr}$). De structuur van het methylcomplex werd opgelost met éénkristal Röntgendiffractie. Er werd gevonden, dat excitatie in de laagste absorptieband in oplossing leidt tot homolytische Rh–R-bindingssplitsing. Deze fotoreactie treedt op na crossing van de optisch geëxciteerde XLCT-- ($X = 1$) naar de reactieve SBLCT-toestand. Voor het iPr-complex wordt de homolyse waargenomen bij langere-golflengtebestraling dan voor het methylderivaat, hetgeen aantoont dat in het eerste geval de SBLCT-toestand lager in energie is.

Uit het voorgaande is duidelijk dat nu veel meer bekend is over SBLCT-toestanden en -overgangen in $d^6$ metaal–diiminecomplexen dan aan het begin van dit promotieonderzoek. Rest de vraag langs welke lijnen onderzoek naar SBLCT-toestanden en -overgangen voortgezet zou kunnen worden.

De belangrijke aspecten van deze complexen zijn hun fotolabiliteit en emissie-eigenschappen. Door het $\alpha$-diimine ligand te variëren, konden de complexen vrijwel fotostabiel worden gemaakt, terwijl tegelijkertijd de energie van de SBLCT-toestand zodanig werd verlaagd dat NIR-emissie werd waargenomen. Helaas was deze emissie nogal zwak in een lage-temperatuurglas en niet waarneembaar in oplossing. Hoewel theoretische resultaten enige aanwijzingen geven over de redenen voor dit gedrag, dat niet gevonden wordt voor complexen met een laagste MLCT-toestand, zou verder onderzoek zich allereerst moeten richten op dit probleem. Dit kan geschieden door met behulp van ultrasnelle tijdsopgeloste-
absorptiemetingen informatie te verkrijgen over de niet-stralende vervalkanalen die de efficiëntie van de emissie van deze complexen verlagen. De resultaten van deze studies zouden kunnen aangeven hoe dergelijke complexen met een laagste SBLCT-toestand gehermodelleerd moeten worden, teneinde niet alleen fotostabiel te zijn en een zeer lange levensduur te bezitten, maar ook met hoge kwantumopbrengst te emitteren. Dergelijke tijdsopgeloste metingen zouden ook aan kunnen geven welke factoren de vorm bepalen van de potentiële-energiecurves van de SBLCT-toestand en de barrière voor dissociatie in het geval van fotoreactieve complexen.

Recente ultrasnelle electronische absorptie- en tijdsopgeloste FT-EPR-metingen aan metaal-alkyl gebonden complexen tonen aan dat snelle bindingshomolyse kan optreden vanuit de Franck-Condon toestand. In tegenstelling tot deze verbindingen hebben de SBLCT-toestanden van vele van de in dit proefschrift beschreven complexen een potentiële-energieoppervlak met een duidelijk minimum. Verdere (ultrasnelle) tijdsopgeloste spectroscopische (UV/Vis, IR, FT-EPR) studies zouden licht moeten kunnen werpen op de dynamica van de aangeslagen toestand van zulke systemen.

Naast het ontwikkelen van nieuwe systemen die sterker emitteren vanuit hun SBLCT-toestand is het belangrijk te weten welke andere systemen gekarakteriseerd worden door een laagste SBLCT-toestand. Van de vele studies die al gedaan zijn hadden alle, behalve die van de \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\) clusters, betrekking op \(d^8\) Mn, Re, Ru, Os of Pt complexen met \(\alpha\)-diimine-liganden. Verwacht mag worden dat SBLCT-toestanden niet beperkt zijn tot deze complexen. Opvallend afwezig zijn de complexen van de groep 9 overgangsmetaalatomen. Hoewel twee nieuwe rhodium-alkyl complexen werden beschreven in hoofdstuk 6 waarvoor het optreden van een SBLCT-toestand werd bewezen, heeft de laagst-energetische electronische overgang XLCT-(\(X = I\)) en geen SBLCT-karakter. SBLCT-systemen zouden ook niet beperkt moeten zijn tot complexen van \(\alpha\)-diimines, omdat vele andere liganden, zoals bijv. porfyriines, ook laagliggende lege orbitalen bezitten.

Tenslotte, diffunderen de radicalen gevormd door de homolysereacties van de in dit proefschrift beschreven metaal-diiminecomplexen met twee \(\sigma\)-gebonden liganden, uit elkaar, hetgeen de fotoreacties irreversibel maakt. Bij de bovengenoemde Os-clusters, worden de radicalen bijeengehouden in een biradicaal door een Os(CO)_4-fragment, hetgeen leidt tot interessante secundaire reacties. Er zouden systemen ontwikkeld kunnen worden waarin het \(\sigma\)-gebonden ligand verbonden is met het \(\pi\)-acceptorligand of met een co-ligand, wat tot soortgelijke vorming van biradicalen en tot interessante vervolgreacties zou kunnen leiden.
Dankwoord

DANKWOORD


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LIST OF PUBLICATIONS


