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TAILOR MADE COORDINATION COMPOUNDS FOR PHOTOCHEMICAL PURPOSES.

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Abstract

An account of the strategies for the synthesis of coordination compounds with interesting photophysical and photochemical properties is given. Ru(II)-diimine complexes have been developed with various absorption and emission characteristics and for special chemical stability of the excited state species. The isomer problem, encountered in the synthesis of polynuclear complexes, which are candidates for Photochemical Molecular Devices (PMD), is attacked by using enantiomerically pure chiral building blocks or chiragen ligands, which form metal complexes with predetermined helical chirality. Cyclometallating ligands with Pt(II) and Pd(II) can be designed, so that the photochemically induced oxidative addition reactions lead to compounds of special interest, especially from the stereochemical point of view.

1. Introduction

The interest in photochemistry and photophysics of coordination compounds has been an important driving force for the synthesis of new metal complexes in recent years. In a collaborative effort with other laboratories, i.e. the groups of *V. Balzani in Bologna, Italy, F. Vögtle in Bonn, Germany, the late G. Gliemann in Regensburg, Germany, H. Yersin in Regensburg, Germany, and H.U. Güdel in Bern, Switzerland*, we have synthesized during the past ca. 12 years a number of new complexes, which are especially designed as objects for research in the field of photochemistry and photophysics. In the present paper, an account of the strategies of syntheses of these compounds is given, together with an outlook for future developments. The main emphasis in our group was

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to develop new compounds in the 4d^6 Ru(II)-diimine family on the one hand and in the class of 4d^8 and 5d^8 Pd(II) and Pt(II)-cyclometallated complexes on the other hand.

2. Ruthenium(II)-Diimine Complexes: From $Ru(bpy)_3^{2+}$ to Supramolecular Species.

The exceptional photophysical and photochemical properties of $Ru(bpy)_3^{2+}$, especially as a Light Absorption Sensitizer (LAS), are a challenge to the synthetically interested coordination chemist, raising the question, whether $Ru(bpy)_3^{2+}$ is real a unique case and secondly, whether it could be altered in a way to be optimized with respect to certain of its molecular properties.

2.1. Tuning of the energy of the First Excited MLCT-State

A first goal was the tuning of the energy of the first excited MLCT-state, giving rise to the 452 nm ($\varepsilon = 10000$) absorption maximum in $Ru(bpy)_3^{2+}$. A large number of tris-diimine complexes - homoleptic, bis-, and tris-heteroleptic - was synthesized by us and by other groups. A sample collection of diimine ligands used is depicted in scheme 1.

A typical result for a bis-heteroleptic complex is shown in Figure 1. It demonstrates the fact, that the MLCT-absorptions seem to be localized in terms of their assignment to an electron transfer to a specific bidentate diimine ligand. Through the synthesis of mixed ligand complexes with various diimine ligands a large part of the visible spectrum can be covered by the MLCT absorptions. A rather complete account of the published earlier results (up to 1987) was given in a review article in this journal [1].

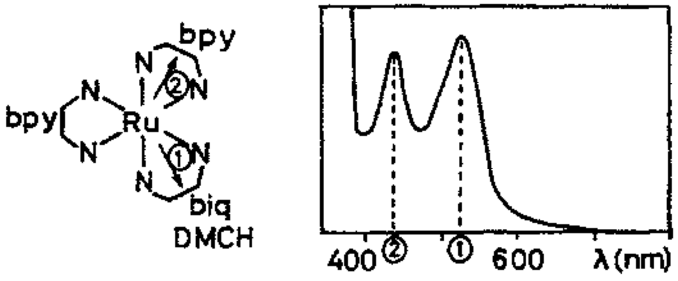
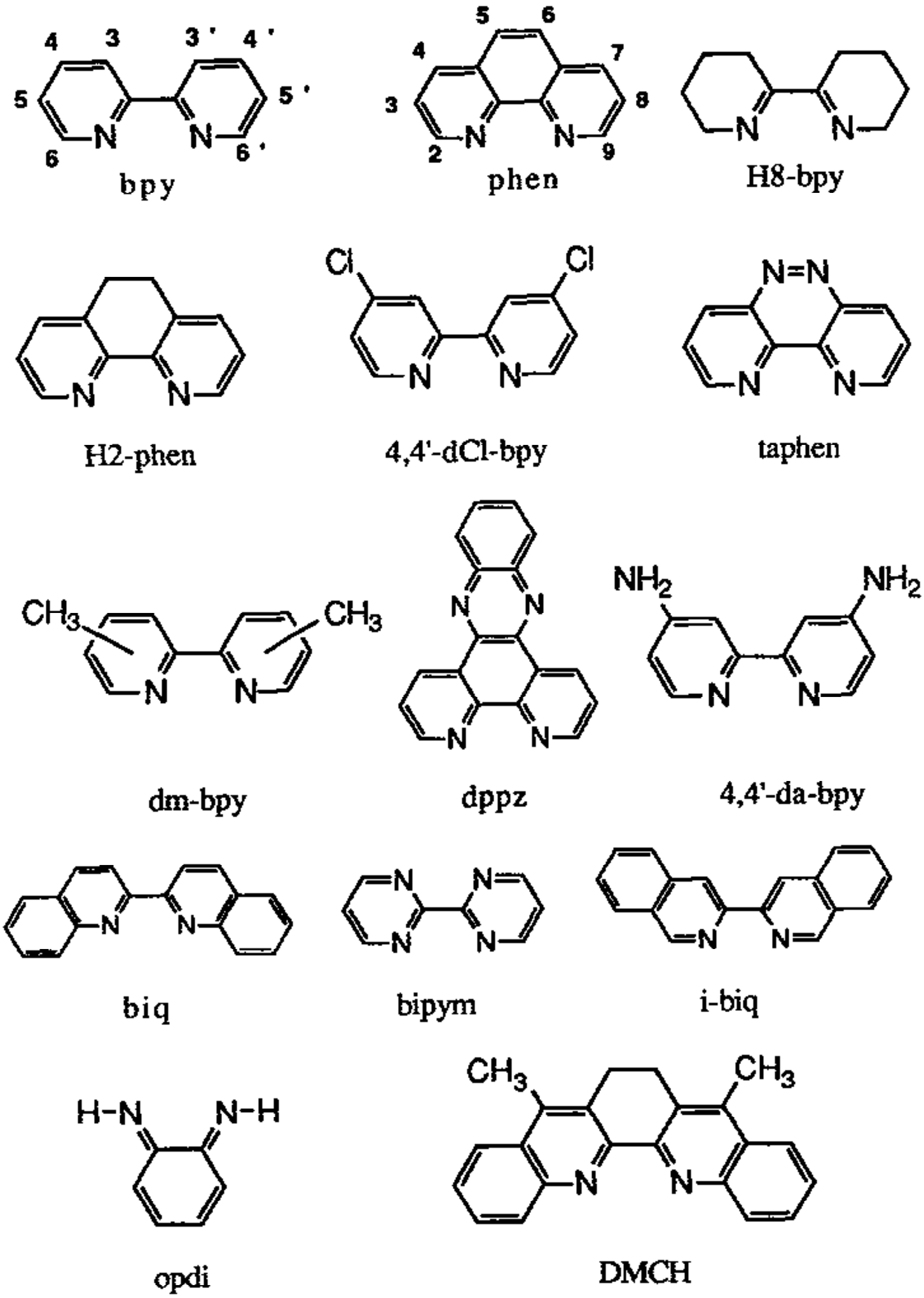


Figure 1. Typical absorption spectrum of a mixed ligand Ru(II)-complex, with distinct MLCT bands, for two types of ligands.



Scheme 1: Selection of diimine ligands, which cause a large range of absorption energies for the MLCT transitions in Ru(II) complexes.

2.1. Increasing the Photochemical Stability of the LAS

Although $Ru(bpy)_3^{2+}$ has a high photochemical stability [2 - 4], it would be desirable to make it even more stable. It is generally assumed, that the pathway for photochemical alterations (photoracemization and photosubstitution) of the complex goes through a thermally activated step, from the ^{3}MLCT state to a dissociative ^{3}MC (d-d) state. Figure 2 gives the general scheme for this process.

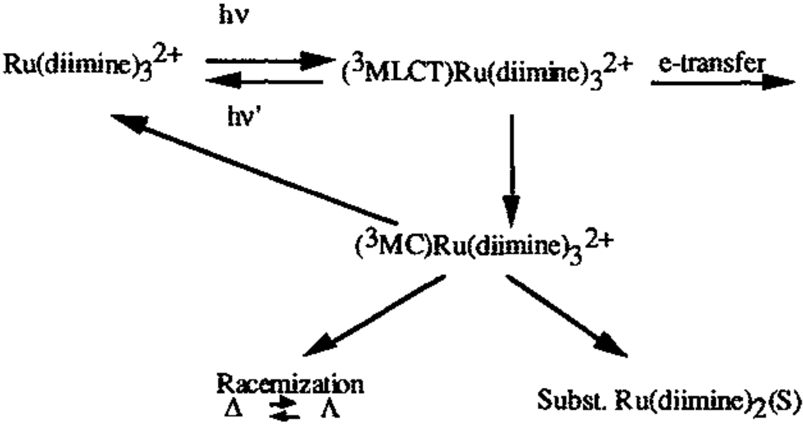


Figure 2. General scheme for photoracemization and photosubstitution processes in $Ru(diimine)_3$ complexes.

There are, in principle, at least two possibilities to increase the photochemical stability of such a complex with respect to photosubstitution and photoracemization: (i) Increasing the energy of the d-d state by using ligands causing a higher ligand field. (ii) Making the ^{3}MC excited state non-dissociative (Figure 3).

The first possibility has been explored in some depth by several authors [5,6,7,8], using cyclometallating ligands (C^N-coordination). The replacement of one nitrogen ligand atom by a negatively charged carbon has, however, profound effects on the properties and the resulting complexes cannot be considered merely as slightly modified $Ru(bpy)_3^{2+}$. The second possibility has been realized by building a cage around the Ru(II)-center [9].

The rigid structures depicted in Figure 4. prevents the dissociation of the complex in the excited state, even if the σ-antibonding ^{3}MC state becomes thermally populated. It was shown, that it suffices to have a half-cage structure (Figure 4), in order to increase the photochemical stability of $Ru(bpy)_3^{2+}$ by about three orders of magnitude.

The synthesis of the cage, and even the half-cage structures is a rather difficult task, and hitherto only small quantities of the complexes have been synthesized. It is not likely that the preparation can be facilitated considerably.

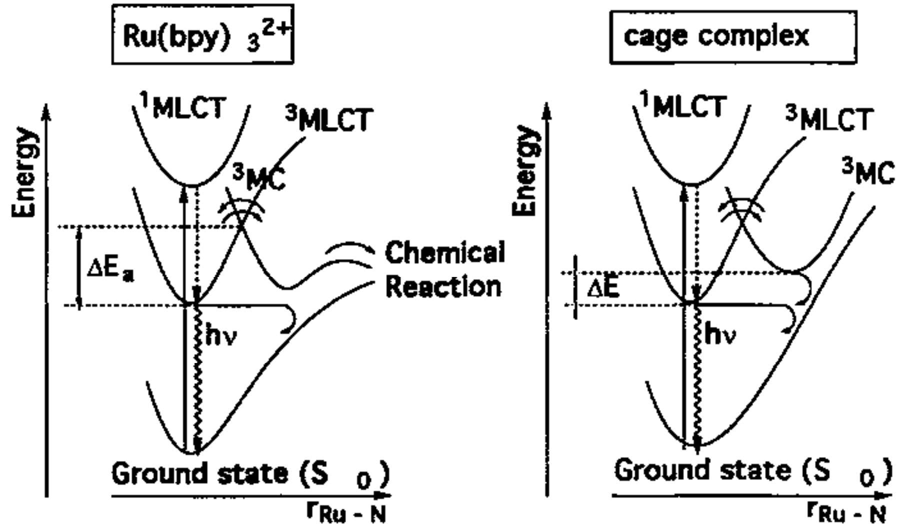


Figure 3. The general energy scheme for tris-diimine complexes with a dissociative, thermally accessible d-d state (left), and the same coordination unit, but with the three bpy-units being held rigidly by a cage ligand (right).

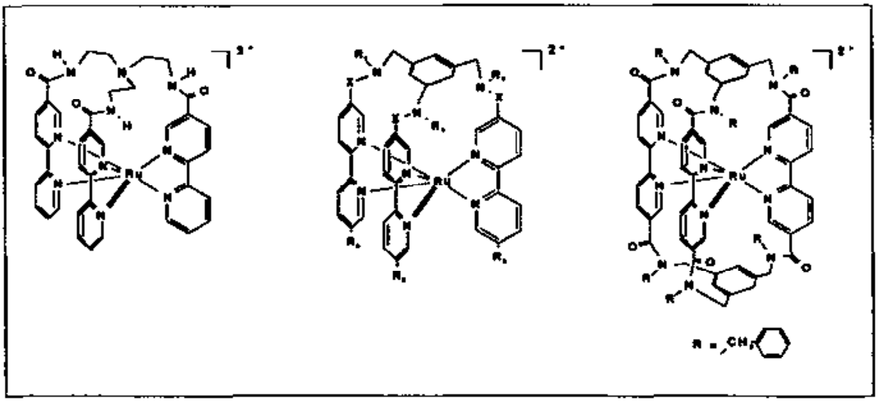


Figure 4. Schematic representation of caged and half-caged complexes of the Ru-tris-diimine type, showing increased stability in their excited states.

2.3. Towards supramolecular systems.

Photochemical Molecular Devices (PMD) require the combination of several functions within one assembly, in order to exhibit new functions, typical for the PMD, not present in one of its components (Figure 5).

The construction principles of such edifices have been described in a recent book [7]. One possibility are *multicenter metal complexes*, which allow for such functions as intramolecular electron and/or energy transfer (Figure 6).

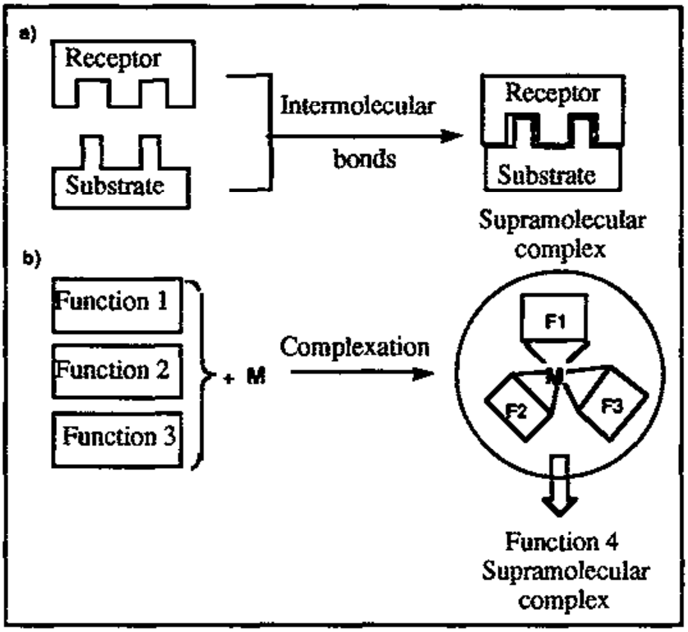


Figure 5. Two representations of supramolecular arrangements of molecular assemblies.

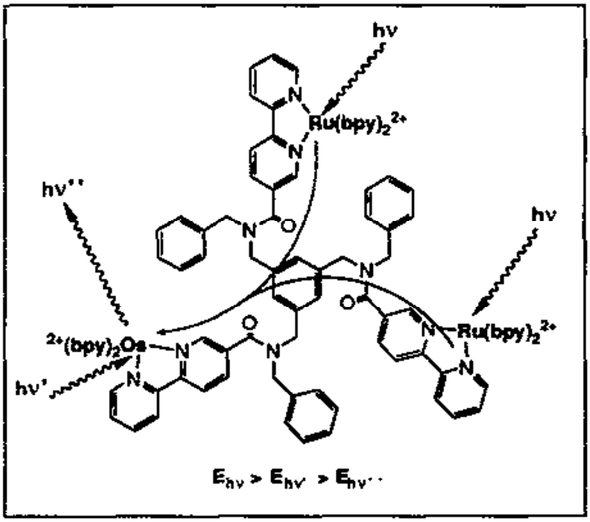


Figure 6. Example of a multicenter, supramolecular species.

The rational synthesis of multicenter metal complexes is a rather new topic in coordination chemistry. Especially tris-diimine complexes pose a considerable problem, since each metal represents a center of helical chirality. This means, that there is a large number of isomers possible ($\leq 2^N$ isomers for a N-center system, the actual number depends on the overall symmetry of the edifice). This large number of isomers prevents in general a detailed characterization of a multicenter system by standard methods (NMR and X-ray structures). ***Separation*** of the isomers is generally ***not feasible***, in view of the very similar properties of the isomeric species. Even if separation were possible, it would mean necessarily a low yield of a given species. The situation is somewhat similar, as if nature had used racemic amino acid to build up proteins. Of course, nature did not use racemic, but rather enantiomerically pure amino acids. One strategy is therefore to use also enantiomerically pure building blocks for polynuclear diimine-type complexes. It has been shown that $Ru(bpy)_2(py)_2^{2+}$ and $Ru(phen)_2(py)_2^{2+}$ are useful building blocks, in which the two py ligands can be substituted with complete retention of configuration [12]. Using these building blocks, isomerically pure dinuclear species were synthesized, so far.. E.g. all three forms (ΔΔ, ΛΛ, and ΔΛ, Figure 7.) of the complex $Ru(bpy)_2(bpym)Ru(bpy)_2^{4+}$ were isolated and completely characterized. The same methods can be applied to complexes of higher nuclearity, in principle.

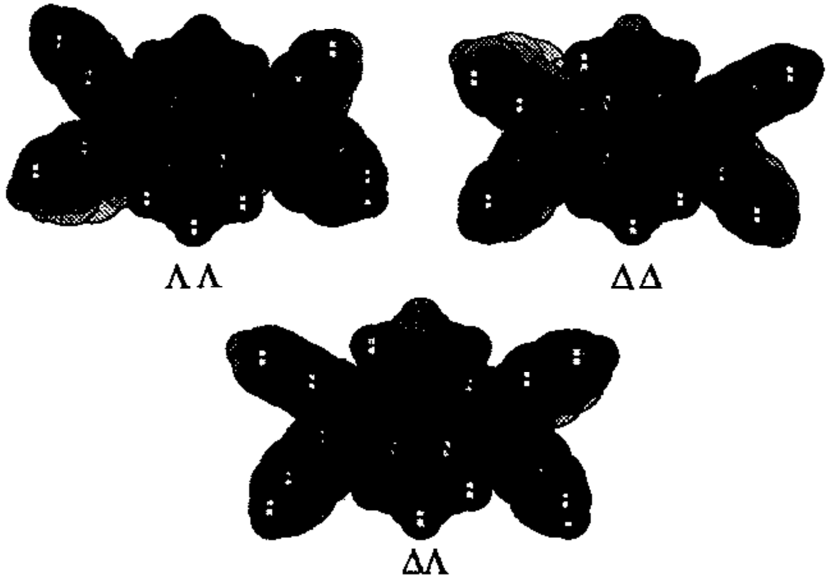
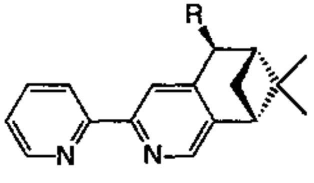
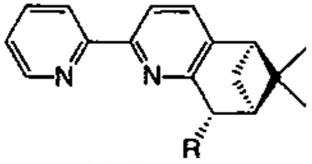


Figure 7. Schematic representation of two diastereomeric forms (ΔΔ, left; ΔΛ, right) of $Ru(bpy)_2(bpym)Ru(bpy)_2^{4+}$ synthesized selectively, using enantiomerically pure building blocks.

Another strategy for the stereospecific synthesis of multicenter systems is the use of building blocks, where the helical chirality is predetermined by a bis-bidentate ligand [14]. We call these ligands the chiragen family, because they generate helical chirality of *one sense only* in an octahedral metal complex. These ligands are derived from new derivatives of bpy, the pinene-bpy [13].



4,5-pinenebpy



5,6-pinenebpy

If two molecules of 4,5-pinenebpy are connected by a bridge, a tetradentate ligand is obtained, in which the six asymmetric carbon centers determine completely the helical chirality (Δ or Λ) of the metal (Figure 7).

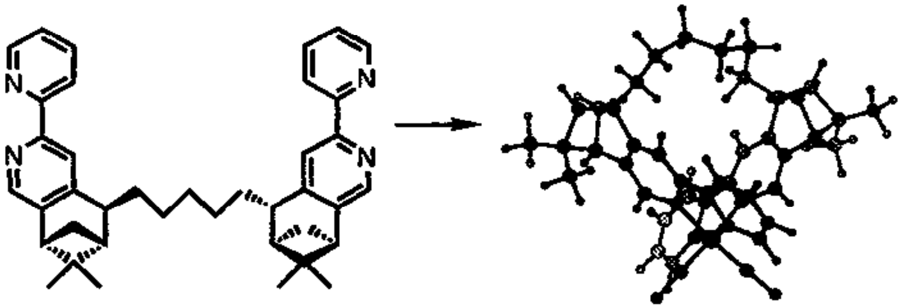


Figure 7. A chiragen (chiragen[5]) ligand (left) and its coordination to a metal ion in a predetermined helicity.

Since the pinenebpy is obtained from natural *chiral pool* molecules in ***high enantiomeric purity***, no separation of enantiomers at any stage of the reaction sequence is necessary. There is even a ***chiral amplification*** upon complexation, because small amounts of the "wrong" enantiomer of the pinenebpy give *meso* bis-pinenebpy ligands, which cannot complex with *one* metal ion. Only very small amounts ($\approx x^2$, if x is the mole fraction of the "wrong" enantiomer) of the chiragen ligand form complexes of the other enantiomeric type (Λ or Δ). The absolute (helical) configuration of the metal complex obtained from pinene of a given configuration has been predicted and later confirmed by X-ray crystallography [14]. Since α-pinene occurs in nature in both enantiomeric forms, but not as a racemic mixture, pinenebpy can be obtained in *both enantiomeric* forms too. Therefore metal complexes with both helical chiralities can be obtained from chiral pool molecules.

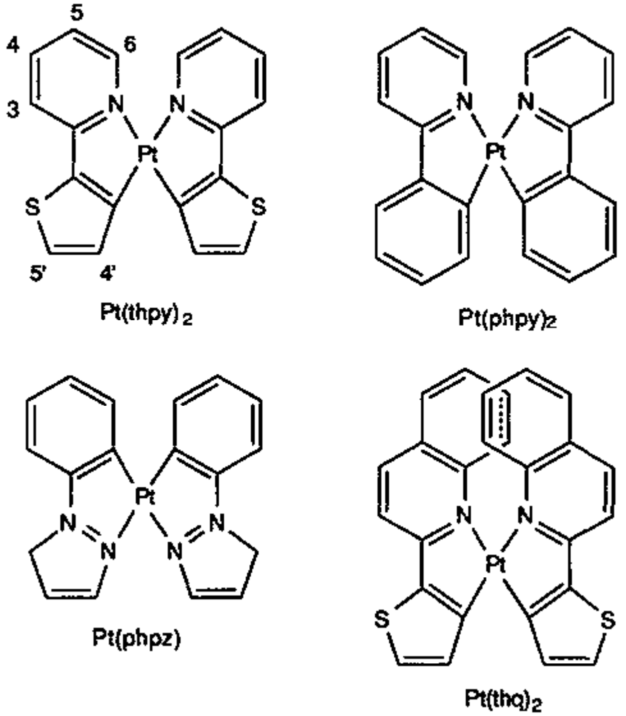
Enantiomerically pure building blocks, either of the $Ru(bpy)_2(py)_2^{2+}$ or the Ru(chiragen)-type can not only be used to make "small" polynuclear complexes. An interesting possibility is the formation of complexes with polymeric ligands, e.g. *polyethyleneimine* with enantiomerically pure building blocks. In this way, chiral polymers can be obtained. It would be interesting to use this material for surface modified electrodes. It may be possible to discriminate in certain cases between substrates of opposite chirality in electron transfer processes at the electrode.

3 Cyclometallated Complexes

Cyclometallated, luminescent Pt(II)-complexes, which can add other molecules in photochemically or thermally induced oxidative addition reactions are another class of complexes, which can be varied in a wide range chemically [17].

C-co-ordinated ligands have, in general, d-d states at relatively high energies, due to the high ligand field strength caused by C as a donor atom. We therefore attempted the synthesis of complexes with several C^N cyclometallating chelate ligands. This turned out to be rather difficult in the $4d^6$ complexes of Ru(II). Other authors have succeeded recently in the synthesis of such species. Homoleptic bis-cyclometallated complexes with the $4d^8$ and $5d^8$ metals Pd(II) and Pt(II), respectively, turned out to be quite accessible, however. The following scheme gives a selection of some complexes, which were synthesized:

Homoleptic bis-cyclometallated compounds



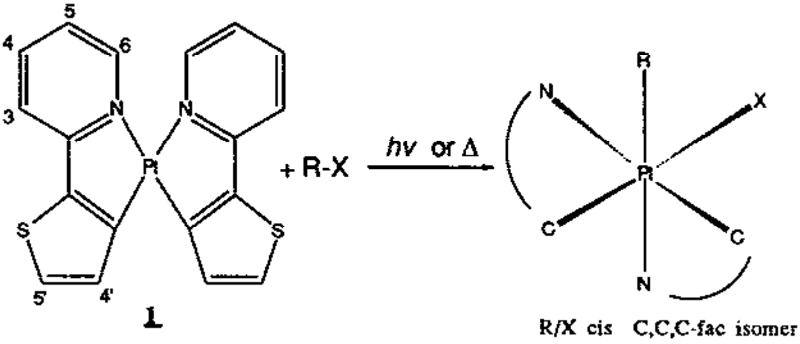
Pt(thpy)$_2$

Pt(phpy)$_2$

Pt(phpz)

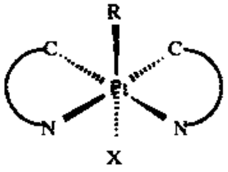
Pt(thq)$_2$

All these complexes show emissions at 77 K, and some (e.g. Pt(thpy)$_2$) even at room temperature. The character of the emissive state is, in general, mainly MLCT, although strong mixture between MLCT and LC has been postulated for some cases. Although these compounds behave *photophysically* somewhat *similar* as the Ru(diimine)$_3$ complexes, their *photochemical* properties are very different. With some organic halides, already in the dark, a relatively rapid oxidative addition takes place. With others, like e.g. dichloromethane, no dark reaction is observed. In this and in other cases, highly efficient *potochemical oxidative addition* reactions are observed, however. Figure[8] gives the overall reaction:

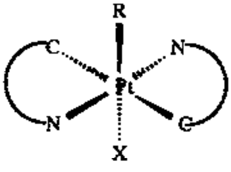


Figure[8]: Photochemical or thermal oxidative addition of organic halides to a bis-cyclometallated Pt-complex.

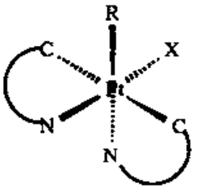
An interesting feature of these reactions is their high stereospecificity. Although there are some exemptions, the reactions are in general stereospecific, giving only one of the five possible stereoisomers:



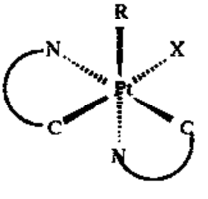
trans - non chiral



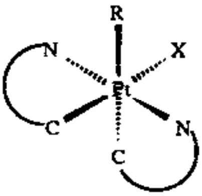
trans - chiral



cis - N,X trans - mer - chiral



cis - fac - chiral



cis - C,X trans - mer - chiral

The mechanism of the POA has been investigated by Balzani and co-workers [18]. A radical mechanism explains the high quantum yield of the reaction.

4. Outlook

The use of molecular building blocks, i.e. *synthons*, so highly developed in organic chemistry, is not a common practice in coordination chemistry. This is not too surprising, in view of the lability of many metal to ligand bonds. Yet, in selected cases, like e.g. the ruthenium complexes, building blocks can be used to "construct" extended, multicenter systems with exactly specified structural features. Such systems have become a subject of current interest for their application in photochemical molecular devices. Since transition metals offer an enormous variety of physical and chemical variety, it is believed, that the synthesis of sophisticated structures containing such elements will become an important area of research in the near future. Synthons containing transition metal units will therefore become a valuable tool in preparative coordination chemistry.

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