

## Two-photon Processes in Organometallic Molecules and Clusters: T-T Absorption of Group IV Metal Complexes

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Triplet – triplet absorption of  $d^0$  metal complexes was for the first time revealed and studied by means of pulse photolysis and electron-exchange (Dexter) resonant energy transfer energy transfer.

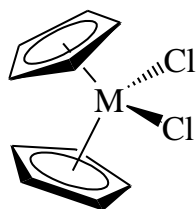
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### 1. INTRODUCTION

Triplet states, based on organometallic compounds, are of special fundamental interest. Phosphorescence study is of importance for triplet state theory advance.

Early-transition metal metallocenes ( $(\pi\text{-L})_2\text{MX}_n$  ( $n = 1\text{--}3$ ) [1] have been a cornerstone in the development of modern coordination organometallic chemistry and catalysis and continue to be a focus of chemical and structural studies giving fresh insights into reactivity, structural preferences, and bonding requirements and even in medical chemistry.



M = Ti, Zr, Hf

Group IV bent metallocenes  $\text{RCp}_2\text{MX}_2$  [ $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ , cyclopentadienyl; M = Ti, Zr, Hf; R – substituent(s) or bridging group(s)] have provided impetus for a new generation of a large family of highly reactive organometallics, for years successfully used in the fields of homogeneous and heterogeneous catalysis [2–3]. Rare ligand-to-metal charge-transfer (LMCT) excited states, based on  $d^0$ -metallocenes of titanium group (Ti, Zr, Hf) [4], were revealed to be highly emissive (*phosphorescent*) and highly long-lived [5–9]. We have obtained first group IV metal complex [bridged zirconocene, namely *rac*- $\text{C}_6\text{H}_{10}(\text{IndH}_4)_2\text{ZrCl}_2$  (*I*)], having high phosphorescence quantum yield ( $\Phi$  up to 0.41) and emissive-state lifetime ( $\tau$  ranging from  $10^{-7}$  to  $10^{-5}$  s. in different aprotic organic media) in fluent solutions at room temperature. [9] In the present contribution, we report results of our on-going study of LMCT excited states based on bridged zirconocene *I* and simpler related unbridged zirconocene  $\text{Cp}_2\text{ZrCl}_2$  dissolved in various organic solvents. In this work, triplet – triplet ( $T\text{--}T$ ) absorption of  $d^0$  metal complexes was for the first

time revealed and studied by means of pulse photolysis and  $T\text{--}T$  energy transfer.

### 2. EXPERIMENTAL

The samples prepared with the use of single crystals *I* were studied. Group 4 metallocene complexes are air and moisture sensitive. Therefore, all measurements and manipulations with these highly reactive molecules were carried out under strictly anaerobic and anhydrous conditions under prepurified inert (Ar or He) atmosphere in flame-dried glassware on a double-manifold high-vacuum line using standard Schlenk technique or on all-glass vacuum line fitted with high-vacuum Teflon stopcocks. All solvents applied were put through a special multiple purification procedure including vacuum distillation from the traces of impurities, oxygen, moisture and also degassed through several freeze-pump-thaw cycles (purity was checked by monitoring the UV-visible absorption and luminescence at 77 K and RT).

Triplet – triplet absorption spectra of the target metallocene systems were obtained with the use of flash-photolysis technique. Steady-state absorption spectra were measured on a Shimadzu UV-2101 PC spectrophotometer. Steady-state emission spectra were recorded with a Perkin-Elmer LS-55 spectrofluorimeter. The photophysical measurements were performed in 1-cm quartz cells at 20 °C.

### 3. RESULTS AND DISCUSSION

$T\text{--}T$  absorption of  $d^0$  metal complexes can be represented at Fig. 1 (where IC stands for the internal conversion and ISC is the intersystem crossing.).

Respectively,  $T\text{--}T$  absorption of  $d^0$  metal complexes was studied with the use of representative complex *rac*- $\text{C}_6\text{H}_{10}(\text{IndH}_4)_2\text{ZrCl}_2$  dissolved in methylocyclohexane (MCH) (the correspondent spectrum is shown on Fig. 1), toluene, *t*-butylmethyl ether (BME),  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,

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$\text{CCl}_4$  and also in THF and 2-methyltetrahydrofuran (MTHF).  $T$ - $T$  absorption maxima at 20°C are located at ~540 nm (in MCH), ~545 nm (in toluene), and ~550 nm (in BME).

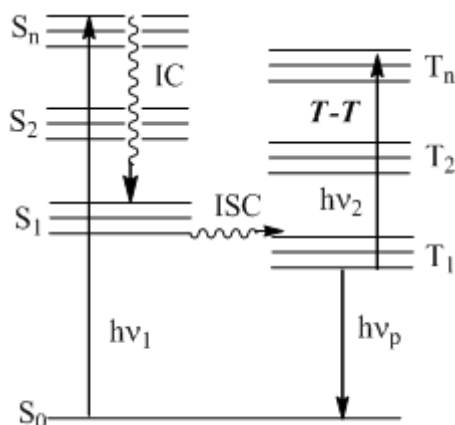


Fig. 1 –  $T$ - $T$  absorption of  $d^0$  metal

At photolysis of the target zirconocene dissolved in chlorine-containing hydrocarbons, THF, and MTFH, a fast photochemical decomposition occurs via dissociation of the sandwich moiety  $\text{C}_6\text{H}_{10}(\text{IndH}_4)_2\text{Zr}<$  and the photolysis products are accumulated not allowing precise characterization for the  $T$ - $T$  absorption of the complex. The rate of photolysis of the complex in chlorine-containing hydrocarbons increases in the sequence:  $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$ . In the similar way, pulse photolysis of  $\text{Cp}_2\text{ZrCl}_2$  solutions was revealed to yield the fast photochemical decomposition already in toluene that does not permit quantitative estimate for  $T$ - $T$  absorption of the simplest zirconocene representative  $\text{Cp}_2\text{ZrCl}_2$ .

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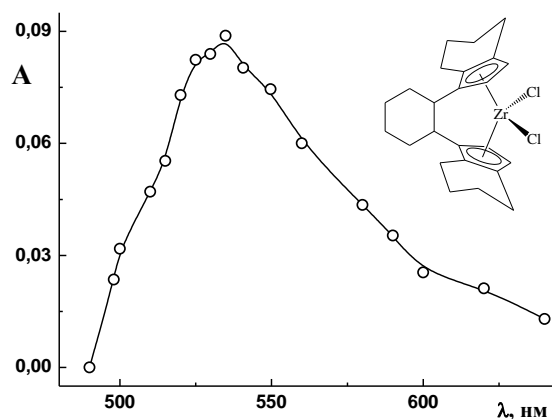


Fig. 2 – Spectrum of triplet – triplet absorption of bridged zirconocene **1**, dissolved in methylcyclohexane, derived at room temperature. The structure of **1** is shown in the insert.

Notably, up-to-date triplet – triplet absorption spectra have been obtained for a remarkable number of organic species, however, at the same time, such spectra, being a power and promising tool for quantitative and qualitative molecular analysis, were reported for a very limited number of organometallic (even one or two-component) systems.

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