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Effect of the coordination sphere of d^0 metallocene on triplet-triplet energy transfer

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The triplet nature of rare long-lived states of d^0 metallocenes formed upon ligand-to-metal energy transfer was confirmed by studies of triplet-triplet charge transfer in biscyclopentadienyl complexes Cp_2MCl_2 (M = Zr (**1**), Hf (**2**)). The interaction between precatalysts and substrates of catalytic polymerization systems, *viz.*, complexes **1** and **2** and unsaturated hydrocarbons (alkenes and dienes), was studied in the region of concentrations close to catalytic values. For organometallic π-complexes, it has been shown for the first time that, in the case of the unsaturated hydrocarbons, the efficiency of energy transfer obeys the Perrin equation. The process occurs at distances R_0 close to the diameter of the interacting molecules and is well described by the exchange-resonant mechanism of interaction. In the case of the cyclopentadiene—Cp_2MCl_2 (M = Zr, Hf) systems, R_0 = 14.6 Å. A linear relationship between the critical radius of the quenching sphere R_0 and the number of carbon atoms in a linear α-olefin has been revealed for the first time and evidences the formation of a π-complex between the precatalyst and substrate molecules.

Key words: energy transfer, triplet-triplet quenching of luminescence, excited states of organometallic compounds, ligand-to-metal charge transfer, phosphorescence, zirconinum complexes, hafnium complexes.

Traditionally, investigations on photochemistry of coordination and organometallic compounds were focused on search for long-lived excited states and their use in solar energy storage and conversion, data recording and processing, and photocatalysis.[1—6] The presence of transition metal ions in coordination molecules causes partial or complete removal of the spin-forbidden nature due to a strong spin-orbital interaction and also results in nonradiative energy degradation due to vibrational coupling because of high convalence of metal—ligand bonds. In contrast to various phosphorescent states based on organic molecules, long-lived radiative states based on coordination (especially organometallic) compounds are virtually unknown; the properties of compounds of late transition metals are mainly studied.[1—6] No systematic studies of excited states formed due to the ligand-to-metal charge transfer (LMCT) are known.[4—8]

Metallocene complexes play an important role in the catalytic production of polyethylene and polypropylene and activation of small inert molecules (N_2, CO, CO_2, and others). Based on bent metallocenes of Group IVB elements, *viz.*, 16-electron complexes of d^0-metal ions with polyhapto and monodentate ligands* $(\pi\text{-L})_2M^{IV}X_2$ (X is halogen, alkyl, *etc.*), a large number of practically valuable systems were proposed (*e.g*, catalysts for olefin polymerization[9—12]).

For the metallocene triad $Cp_2M^{IV}X_2$ (M = Ti, Zr, Hf) we developed an experimental approach to essessment of the properties and estimation of the relative energies of the frontier MOs (HOMO, LUMO) of organometallic π-complexes[8,13—16] and started systematic investigations of rare radiative LMCT states of compounds of this class. The purpose of the present work is to study the mechanism of triplet-triplet (T—T) energy transfer in systems based on d^0 metallocenes of Group IVB elements and the interaction between the organometallic d^0 complexes (main components of the Ziegler—Natta catalysts) and unsaturated hydrocarbons (UHCs). Energy transfer between organic molecules and transition metal compounds only recently has become an object of investigation, and the effect of the structures of organic and coordination molecules of energy donors and acceptors on the efficiency of nonradiative T—T energy transfer is rather poorly studied.

Experimental

All measurements and preparation of samples of highly reactive metallocene complexes were carried out under anaerobic and anhydrous conditions in a high-purity inert gas (Ar, He)

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* η^5-Coordination of π-ligands is most stable.

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pre-purified from oxygen and water traces by passing through columns with activated molecular sieves and the catalyst in evacuated and annealed glassware on a high-vacuum line using the standard Schlenk technique. All solvents were purified and thoroughly dried followed by distillation and degassing using multiple freezing—evacuation—thawing out cycles. This procedure was continued until a gas pressure above the liquid after thawing out and repeated cooling of less than $5 \cdot 10^{-3}$ Torr. The solvents were stored *in vacuo* or under an inert gas with a drying agent (sodium—potassium alloy or molecular sieves) and transferred *in vacuo* from the drying agents prior to use. All unsaturated hydrocarbons were additionally purified, thoroughly dried, and distilled immediately before use. Purity of solvents and unsaturated hydrocarbons was monitored by recording the absorption and luminescence spectra at different UV excitation wavelengths ($\lambda_{exc} \geq 250$ nm for saturated hydrocarbons and $\lambda_{exc} \geq 300$ nm for most unsaturated and aromatic hydrocarbons) at room temperature and 77 K. Samples of the complexes were pre-purified by recrystallization from the mother liquor or by vacuum sublimation at moderate temperatures. The low content of the complexes in the samples was used (10^{-5}—10^{-4} mol L^{-1}) to avoid concentration effects.

Absorption spectra were recorded on a Hewlett Packard 8451A Diode Array spectrophotometer. Luminescence spectra were measured on a spectrofluorimeter described earlier[17] using quartz optical cells and ESR tubes. Low-temperature spectra were obtained using a quartz optical Dewar sample holder of special construction excluding condensation of moisture. The experimental setup and basic theoretical models used were described previously.[17,18] Energy transfer between molecules and the cooperative effects were studied in glassy solutions of individual unsaturated hydrocarbons and in two-component UHC—methylcyclohexane solutions at 77 K.

Results and Discussion

Properties of radiative states of metallocenes and their deactivation by unsaturated hydrocarbons in hydrocarbon glasses. Titanium, zirconium, and hafnium in the oxidation state 4+ are weak oxidants, and their oxidative ability decreases in the order Ti ≫ Zr > Hf. The absorption spectra exhibit the LMCT bands predominantly in the UV region and in the high-energy part of the visible spectral region. Earlier[13—15] we explained the nature of the first long-wavelength absorption band in the spectra of the d^0 metallocenes as a result of charge transfer between the frontier orbitals (for instance, for the metallocene π-complexes with the dichloride σ-ligands ($(\pi\text{-L})_2\text{MCl}_2$: $[(\pi\text{-L})_2{}^{2-}\text{M}^{4+}\text{Cl}_2{}^{2-}] \rightarrow \rightarrow [(\pi\text{-L})_2{}^{-}\text{M}^{3+}\text{Cl}_2{}^{2-}]^*$). This is a rare case when the radiative states of organometallic compounds are formed by the charge transfer from the ligand and predominantly localized on the metal ion. In the luminescence spectra of solutions of the Cp_2MCl_2 triad (M = Ti, Zr, Hf), a weakly resolved vibrational structure appears at 77 K. The spectral shape is independent of the exciting wavelength, because the rate of internal conversion from the highest singlet states is much higher than that from the S_1 state to S_0. The low molar absorption coefficients of the absorption band of Cp_2MCl_2 ($\varepsilon \approx 200$ for Ti, 950 for Zr, and 1200 L mol^{-1} cm^{-1} for Hf) indicate that the coupled radiative transition is forbidden.[19] If radiation was caused by the $S_1 \rightarrow S_0$ transition (fluorescence), then the quantum yields would be low, because nonradiative processes should prevail in this case. In our case, the quantum yields are close to unity, and the luminescence lifetimes change from hundreds of microseconds to several milliseconds at 77 K (they are among the longest lifetimes for the known metal-containing molecules). Therefore, we suppose that the radiation is caused by the spin-forbidden transition $T_1 \rightarrow S_0$ (phosphorescence).

In the present study, we used the triplet-triplet energy transfer technique and obtained a direct evidence for the triplet nature of the radiative excited states in the systems based on the metallocenes of Group IVB elements*; we also revealed that the efficiency of luminescence quenching depends on the structure of the energy acceptor.

To a first approximation, the nonradiative energy transfer should depend on the position of triplet levels of the donor (D) and acceptor (A). Thus, the T—T energy transfer described by the scheme

$$D^* \text{ (triplet)} + A_0 \text{ (singlet)} \rightarrow D_0 \text{ (singlet)} + A^* \text{ (triplet)}$$

is efficient if $E_{D^*(\text{triplet})} > E_{A^*(\text{triplet})}$.

We determined the energies of the T_1 levels of UHCs from the data on quenching of phosphorescence of aromatic amines and other aromatic compounds in methylcyclohexane (MCH) upon the addition of different amounts of the UHCs: 24 700 cm^{-1} < E_T < 25 700 cm^{-1}. For cyclopentadiene (C_5H_6, CpH) E_T < 24 700 cm^{-1}. All UHCs studied have high-energy singlet states, are characterized by a large S_1—T_1 splitting,[19,22,23] do not participate in redox and electron transfer reactions under the experimental conditions, and, hence, can be used as triplet acceptors. We have previously[8,16] estimated the energy of the triplet level of the donor E_{0-0} for Cp_2MCl_2 (M = Zr^{4+}, Hf^{4+}) in 3-methylheptane: 24 300 cm^{-1} for Zr and 26 300 cm^{-1} for Hf. Note that the energy of the T_1 level of metallocenes increases considerably upon heating polycrystalline metallocene samples in glassy hydrocarbon solutions to room temperature (E_{0-0} increases up to ~1500 cm^{-1}).** Therefore, the condition $E_{\text{Cp}_2\text{MCl}_2{}^*(\text{triplet})} \geq E_{\text{HYB}^*(\text{triplet})}$ can be fulfilled in the first approximation. Indeed, at 77 K we observed the complete or partial quenching of luminescence in the systems containing Cp_2MCl_2 (M = Zr^{+4}, Hf^{+4}) as donors (D) and UHCs containing one ((a)cyclic olefins) or two ((a)cyclic dienes) C=C bonds as triplet energy acceptors (A). Good

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* Preliminary results of the present study have been published previously.[20,21]

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agreement between the results obtained in glasses of pure UHC quenchers and their mixtures with MCH shows that in most systems without strong specific interaction between the UHC and the medium (aromatic or unsaturated hydrocarbons) the energy transfer is not limited by the association of the UHC quencher molecules with hydrocarbon solvents.

Thus we found quenching of luminescence for the compounds of Group IVB metals and the class of organometallic π-complexes. Direct experiments showed that metallocenes of the Group IVB elements have triplet lowest radiative states and their long-lived luminescence is phosphorescence.

Notably, the quenching of luminescence of the d^0 metallocenes by aromatic compounds in the case of the complexes of Group III metals was observed for Cp_2ScCl_2, but no correlation with the energies of the triplet states of the acceptors was found.[24] Moreover, the luminescence was quenched by all aromatic acceptors used with high triplet states ($E_{A^*(triplet)} \geq E_{Cp_2MCl_2(triplet)}$). This fact was ascribed to the formation of some nonluminescent complexes $[Cp_2ScCl_2 \cdot A]$, and no T—T energy transfer occurred between the d^0 complexes of scandium and triplet energy aromatic acceptors.

Exchange-resonant mechanism of energy transfer. In the case of the triplet energy acceptors under study (linear α-olefins, cyclohexene, cyclopentadiene, R(+)-limonene), the efficiency of energy transfer from the excited states of hafnocene obeys the Perrin equation $q_0/q = \exp(NV[A])$ (q_0 and q are the quantum yields of luminescence of the donor in the absence and in the presence of quencher A, $N = 6.02 \cdot 10^{20}$, $V = 4/3\pi R^3$ (cm^3), and R is the effective radius of the quenching sphere of the volume V). The process occurs at distances R_0 close to the diameter of interacting molecules and is well described by the exchange-resonant mechanism of interaction. The concentration plots of the efficiency of hafnocene luminescence quenching by linear α-olefins in MCH at 77 K in the coordinates of the Perrin equation are shown in Fig. 1. The efficiency of quenching of luminescence of zirconocene and hafnocene is plotted *vs.* cyclopentadiene (CpH) concentration in Cp_2MCl_2—CpH—MCH systems in Fig. 2 (product NV is 7.8; the critical radii of energy transfer between the Cp_2MCl_2 (M = Zr, Hf) and CpH molecules are 14.6 Å). These experiments confirm the triplet nature of the radiative LMCT excited states for the Group IVB metallocenes.

It is of interest that in homologous $Cp_2Zr^{IV}Cl_2$ (electronic configuration of the Zr atom in the oxidation state 4+ is [Kr]$4d^0$) and $Cp_2Hf^{IV}Cl_2$ (electronic configuration of the Hf atom is [Xe]$4f^{14}5d^0$) complexes the critical radius of energy transfer is the same. At the same time, some luminescence characteristics of these complexes[8,16] (for instance, the lifetimes at 77 K are 2 ms (Zr) and ~0.3 ms (Hf)) and the catalytic[9,10] and redox[13,14] properties differ appreciably due to the strong spin-orbital interaction for Hf compared to that for Zr (see Ref. 20).

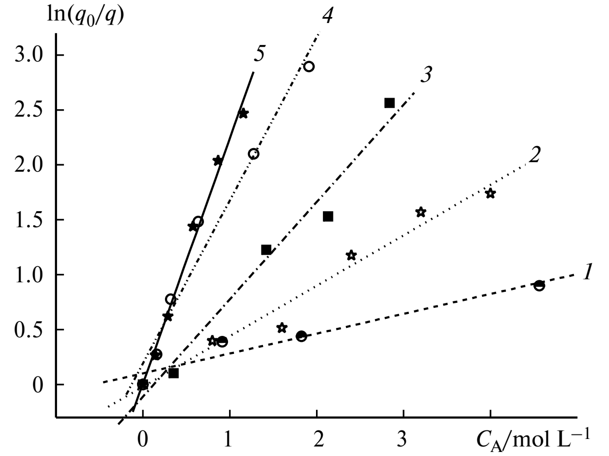


Fig. 1. Concentration plots of the efficiency of hafnocene luminescence quenching by triplet acceptors, *viz.*, linear α-olefins (n = 5—9), in methylcyclohexane at 77 K in the Perrin equation coordinates: *1*, pent-1-ene; *2*, hex-1-ene; *3*, hept-1-ene; *4*, oct-1-ene; and *5*, non-1-ene.

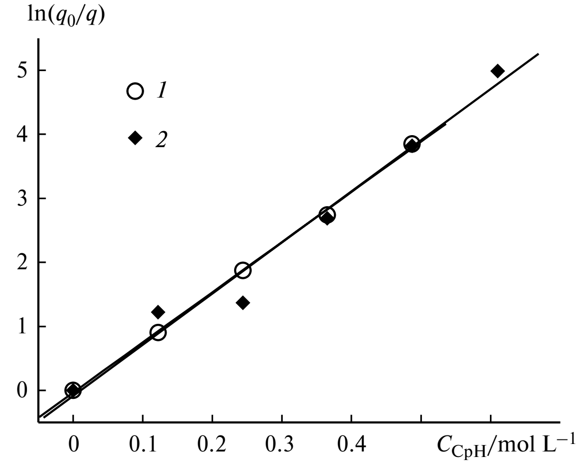


Fig. 2. Concentration plots of the efficiency of quenching of Cp_2ZrCl_2 (*1*) and Cp_2HfCl_2 (*2*) luminescence by cyclopentadiene in glassy solutions of MCH at 77 K in the Perrin equation coordinates.

Coordination interaction between linear α-olefins and hafnocene. The dependence of the critical radius of the T—T-energy-transfer sphere on the size of the quencher molecules was studied with use of linear low-molecular-weight α-olefins. For this purpose, we studied five systems with Cp_2HfCl_2 as the donor and five olefins (C_5H_{10}—C_9H_{18}) that can form glassy solutions (at least in a mixture with well vitrifying saturated hydrocarbons) and are appropriate for measuring the quantum yield of luminescence at 77 K. The experimental R_0 values (obtained from the Perrin dependences, see Fig. 1) are close to the chain lengths of the corresponding α-olefins in the following homological order: 4.2 Å for pent-1-ene, 5.7 Å for

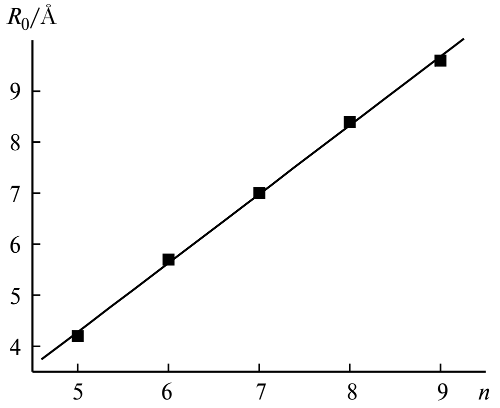


Fig. 3. Dependence of the critical radius of the energy-transfer sphere R_0 on the number of carbon atoms n in quenching molecules of linear α-olefins (C_5H_{10}—C_9H_{18}).

hex-1-ene, 7.0 Å for hept-1-ene, 8.4 Å for oct-1-ene, and 9.6 Å for non-1-ene. When the hydrocarbon chain of the homologous energy acceptor elongated, the critical radius of the T—T-energy-transfer sphere R_0 increased by ~1.35 Å for each —CH_2— unit, which is shown in Fig. 3.

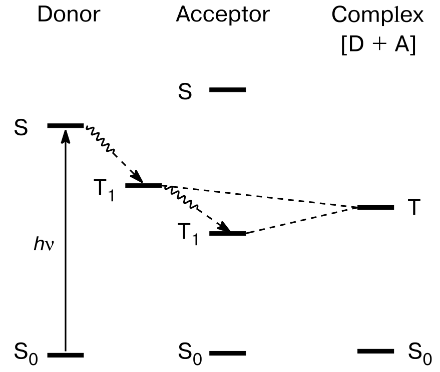
Thus, in the present work, for the Cp_2HfCl_2—C_nH_{2n} (n = 5—9) systems we revealed for the first time the linear dependence of R_0 on the number of carbon atoms and, correspondingly, chain length of linear α-olefins: $R_0(Å) = -2.47 + 1.35n$ (see Fig. 3). In our opinion, this indicates the formation of π-complexes in the ground state between molecules of the main component of the metallocene catalysts for polymerization and unsaturated substrate in solution. Evidently, the coordination of olefin with a metal ion is accompanied by weakening of the double bond in an UHC molecule and a change in the electron density in the region of this bond (due to partial overlap of the nonbonding vacant d-orbital of the metal ion and the occupied π-orbital of the UHC). In this case, a strong influence of steric factors on coordination should be expected. Note that examples of inner-sphere coordination of UHCs with transition metal compounds to form highly labile π-complexes are known in metal complex catalysis. However, relatively stable π-complexes of olefins are known for the late transition metals, in particular, Group VIII metals.

These and other peculiarities can appear in olefin polymerization by the Ziegler—Natta catalytic systems based on complexes of Group IVB metals.

Coordination interaction between UHCs and d^0 metallocenes (zirconocene, hafnocene). We observed the violation of the T—T-energy-transfer law ignoring specific interactions between energy donor and acceptor molecules of the type $D + A \rightleftharpoons [D \cdot A]$. Quenching of luminescence of the zirconium and hafnium π-complexes was found in glassy solutions, which seems to be due to chemical interactions. (The absorption spectra of the metallocenes have very broad structureless bands[8,16] and are much less informative than the luminescence characteristics.) The interaction of the metallocenes with unsaturated triplet acceptors revealed unexpected features: none of the UHCs, except for cyclopentadienes, quenches Cp_2ZrCl_2 luminescence. Sterically hindered 3,3-dimethylbut-1-ene quenches liminescence of neither Cp_2ZrCl_2 nor Cp_2HfCl_2, whose triplet level is higher than E_T of all the UHCs used. On the one hand, in some cases the lifetimes and luminescence spectra of the metallocenes remain unchanged in glassy solutions with the UHCs. On the other hand, we observed considerable shifts of the luminescence spectra (for instance, in the system with Cp_2ZrCl_2) without any decrease in the quantum yield. For example, the introduction of R(+)-limonene into a solution of Cp_2ZrCl_2 in MCH results in a substantial nonmonotonic blue shift of the luminescence spectra to 1000 cm^{-1} at the monomer content ranging from 5 to 50 vol.%. Meanwhile, in the presence of 0.5—1 vol.% R(+)-limonene, the luminescence spectra of the Cp_2ZrCl_2—limonene—MHC system almost coincide with the spectrum of Cp_2ZrCl_2 in pure MCH. The presence of compounds able to coordination to transition d^0-metal ion in the interacting system results in the competition with UHC for the site in the coordination sphere, which can hinder the insertion reaction. The existence of similar effects in a solid glassy matrix at 77 K implies that the $[Cp_2ZrCl_2 \cdot \text{limonene}]$ complexes are formed already in the ground state but the complexation constants are low.

Presumably, the coordination interaction of the metal complex with the UHC affords *in situ* new equilibrium donor—acceptor complexes of the general formula $[Cp_2M(IV)Cl_2 \cdot nUHC]$ (see Scheme 1).

Scheme 1



We assume the inner-sphere coordination of the unsaturated quencher UHC through the C=C double bond with the metal atom of the complex resulting in the formation of zirconium(IV) and hafnium(IV) complexes with π-extra-ligand(s). Outer-sphere coordination between the electronic systems of aromatic and σ-donating Cl^- ligands of the metallocene and unsaturated bonds of the quencher can also be assumed (for instance, through stacking of aromatic π-systems by the planes). The above results show that, in some cases, new luminescent complexes were formed *in situ* from the metallocenes and UHCs due to a reduction (to a greater or lesser extent) of the order of the C=C double bond and, as a consequence, an enhancement of the triplet level of the coordinated quencher (UHC) molecule. The theory of metal complex catalysis assumes the existence of a weak inner-sphere coordination of olefins by related organometallic species through[9] the interaction of the frontier orbitals of the molecules: the HOMO of the monomer and LUMO of the organometallic catalytic species. This type of coordinative interaction has recently been proposed in an NMR study of the reactions of olefin insertion into the M—H bond in the series of the substituted dihydride zirconium and hafnium metallocenes (in the region of high concentrations).[25] The study of the phenomenon of monomer coordination by the photophysical methods can play the key role in understanding the catalytic polymerization of unsaturated compounds by organometallic complexes, in particular, d^0-metal ion complexes.

Complex formation is usually detected by other methods as well (for instance, UV and NMR spectroscopies) but at concentrations exceeding the catalytic values by at least two orders of magnitude. In this case, intermolecular interactions and processes involving organometallic systems at very low (catalytic) and at higher concentrations should differ, especially in low-polarity organic media being typical of catalysis. Note that the use of T—T energy transfer makes it possible to study interactions in the systems with a very low, almost catalytic content of the Zr and Hf π-complexes.

Thus, metallocenes coordinate with unsaturated molecules due to a combination of two and more types of interactions, such as metal—ligand coordination bonds, stacking of aromatic π-systems, *etc*. The *in situ* formed complexes of the $[Cp_2MCl_2 \cdot n\mathrm{UHC}]$ type can efficiently be protected from tight contact with unbound UHC molecules (this contact is necessary for quenching *via* the exchange-resonant mechanism) by specific isolation in a rigid solvent/UHC cage with retention of the radiative properties in this "cage." (A simple calculation assumes that the spatial separation of the D and A components exceeds 3—4 Å, being at least 10 Å.)

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