Triplet Energy Transfer Insight in Coordination of Unsaturated Hydrocarbons by d^0 Bent Metallocenes (Zr, Hf)

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For a class of π-complexes as energy donors, with the use of highly emissive d^0 metallocenes Cp_2MCl_2 where M = Zr and Hf, it is shown that radiationless triplet energy transfer to unsaturated hydrocarbons in a rigid nonpolar methylcyclohexane (MCH) matrix (where molecular diffusion is absent) obeys the Perrin equation, occurs at radii R_0, being close to the diameter of interacting molecules, and is well described by an electron-exchange resonant (Dexter) mechanism of interaction. Principle correlation between values of the critical radius and a number of C atoms in a linear α-olefin is for the first time reported, viz. R_0 (Å) = −2.47 + 1.35n (obtained for systems [$Cp_2HfCl_2 + C_nH_{2n}$ + MCH] at 77 K). Pronounced blue shifts (up to 1000 cm^{-1}) of low-temperature emission spectra of Cp_2ZrCl_2 in MCH in the presence of dienes, possessing nonconjugated C=C bonds, are observed, thus suggesting inner-sphere diene coordination. In view of the experimental data, inner- and outer-sphere coordinative interaction between the components of catalytic systems for polymerization (d^0 metallocene precatalysts and alkenes and dienes) is rationalized.

1. Introduction

Studies on simple organometallics, whose electronic and vibrational transitions can be properly assigned, provide the much-needed detailed physicochemical understanding of the relationship between ground and low-lying excited states with respect to their reactivity, intramolecular bond-splitting mechanisms, electron and energy transfer properties, and so on.[1] In coordination and organometallic photochemistry, research has traditionally concentrated on the search for long-lived excited states and utilization of their reactions in light energy conversion, information processing, and photocatalysis.[1,2] Luminescent complexes are particularly useful as the loss of luminescence (quenching) can be a sign that the complex is reacting/interacting with another species rather than undergoing radiative decay.

As we know, radiative electronic transition from a triplet excited state (T) to a singlet ground state (S_0) is forbidden by spin selection rules. However, it can be rendered partially allowed by spin−orbit coupling induced by heavy atoms and/or vibrational coupling.[3] Meanwhile, in coordination compounds, radiationless transitions are much more common than radiative transitions. The strong spin−orbit coupling expected for heavy metal ions leads to an efficient intersystem crossing from the singlet excited state to the triplet manifold. However, in the same vein, mixing singlet and triplet excited states via strong spin−orbit coupling, to a great extent, also removes the spin-forbidden nature of the radiative relaxation $T_1 \rightarrow S_0$, yielding emission (phosphorescence). In contrast to phosphorescence of organic molecules, reports on phosphorescence of metal complexes, especially organometallic ones, are limited, and the known instances are mostly referred to late-transition-metal complexes. Thus, excited state lifetimes of coordination compounds, in many cases, invoke the lowest-lying triplet metal-to-ligand charge-transfer state and are governed by the nonradiative deactivation processes. Studies of ligand-to-metal charge-transfer (LMCT) excited states, especially those of triplet origin and based on organometallic species, are very rare.[1,4,5]

Triplet−triplet energy transfer (TET) is the most common and important type of energy transfer involved in chemical and biochemical processes.[3a] Transfer of triplet excited state energy plays a crucial role in the operation of electrophosphorescent and optical memory devices.[6] The actual transfer of excited state energy can occur via different mechanisms. Electron-exchange resonant (Dexter) energy transfer involves the actual exchange of electrons between donor and acceptor and only occurs when their molecular orbitals overlap, and therefore, the ET rate constant exponentially decreases with distance.[3a,7a−c] It should be emphasized that emissive triplet state quenching is, to a much greater extent, associated with chemical interactions than fluorescence quenching or quenching via the dipole-exchange resonant (Förster) mechanism.[7d,e] In fact, the Dexter energy transfer mechanism, responsible for “physical” quenching in the former case, requires orbital overlap between energy donor and acceptor molecules, which is also essential for the formation of chemical bonds. It is worth noting that systematic studies of the relationship between TET and (quasi-)chemical interactions appear to be scarce.

The vast number of interesting, enough simple systems based on group 4 transition metal complexes reported in the literature[1d,4,5,8] (e.g., Ziegler−Natta, metallocene, and post-metallocene catalysts for olefin polymerization[9,10]) provide much inspiration. The interest is not surprising: early transition metal π-complexes have been a cornerstone in the development of modern organometallic chemistry and metal-complex catalysis and continue to be a focus of chemical and structural studies giving fresh insights into reactivity, structural preferences, bonding requirements, and even in medical chemistry.[11] It is known that polymer chain growth in catalytic polymerization processes occurs by coordination of a monomer molecule to a d^0 $(\pi\text{-L})_2MR^+$ metal−alkyl catalytic species,[9,10,12a] although the

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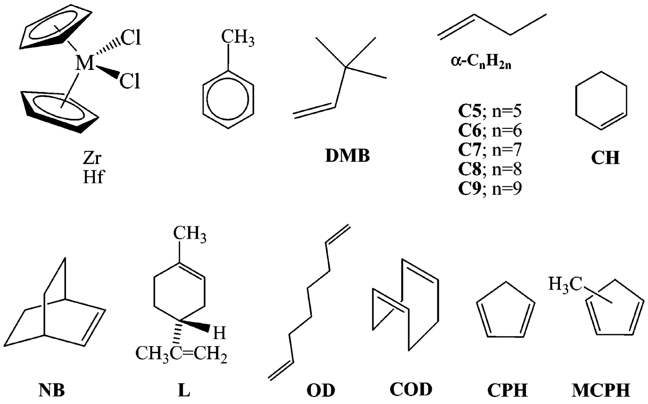
intermediate active species (π-L)$_2$M(R)(monomer)$^+$ have not been detected and the fundamental relation between the precatalyst architecture, catalytic performance, and resulting polymer structure is uncertain.[9] Olefin insertion and β-H elimination reactions for metallocene catalysts remain the subjects of numerous experimental and theoretical investigations, and studies of model d^0 metallocene−monomer complexes are sought to provide insight into basic stages of the catalytic process.[9,12]

Notably, group 4 bent metallocenes (π-L)$_2$MX$_2$ are 16-electron closed-shell complexes made up of a d^0 transition metal and polyhapto-bonded (π-L) and monodentate ligands (X = alkyl, aryl, halide, etc.) The target molecules possess pseudotetrahedral and distorted tetrahedral geometries in their ground states.[4,8,9,13] Such molecules may be taken as belonging to the C_{2v} and lower symmetry groups,[14] and a symmetry treatment gives rise to labeling of the molecular orbitals with the transformation properties but without assignment of a relative order of the energy levels. Computing results (largely at the semiempirical level) evidence this but have been derived for only a few starting homologues of this organometallic family, specifically, for titanocenes and zirconocenes.[4b,j,13] Much debate surrounding the identity and quantities of frontier molecular orbitals (MOs) had focused on the relationship with reactivity and catalytic activity of organometallic molecules, particularly group 4 organometallics.[9,10] Recently, with the use of group 4 metallocenes, we have developed an experimental approach for obtaining redox and optical characteristics of organometallic π-complexes to gain measurable information on the HOMO, LUMO, and HOMO−LUMO gap.[4i,15] Notably, energies of the electrochemical gap ΔE_{redox} and optical HOMO-to-LUMO electron transitions, absorption E_{LMCT} and emission E_{00} in (π-L)$_2$MX$_2$ (Ti, Zr, Hf), linearly correlate, viz. $E_{\text{LMCT}} \propto \Delta E_{\text{redox}}$ and $E_{00} \propto \Delta E_{\text{redox}}$. Replacement of Cl$^-$ with Me$^-$ σ-ligands increases the HOMO−LUMO gap, predominantly by destabilization introduced in the LUMO via Me ligands.[4i] Ligand additivity was demonstrated with the use of (π-L)$_2$MX$_2$ (X = Cl, Me). The origin of the lowest weak transition in a variety of group 4 complexes was justified to be a HOMO-to-LUMO transition; e.g., for (π-L)$_2$MCl$_2$: $[(\pi\text{-L})_2{}^{2-}\text{M}^{4+}\text{Cl}_2{}^{2-}] \rightarrow [(\pi\text{-L})_2{}^{-}\text{M}^{3+}\text{Cl}_2{}^{2-}]^*$. To elucidate further, we initiated a systematic study of the LMCT excited states based on d^0 complexes along group 4 metals.[4i,15,16] Intriguingly, this pure L → M charge transfer between the frontier MOs originates the highly emissive (for Cp$_2$MCl$_2$, where Cp = C$_5$H$_5{}^-$, M = Zr (**Zr**) and Hf (**Hf**): $\Phi_{\text{LUM}} = 1$ at 77 K), extremely long-lived (τ in the range of milliseconds at 77 K) states in group 4 metallocenes.

In the present study, we investigate energy transfer mechanisms between π-complexes **Zr** and **Hf** as the highly emissive donors and unsaturated hydrocarbons (UHCs) as the nonphosphorescent triplet energy acceptors (Chart 1). In these systems, chromophores **Zr** and **Hf** can be selectively excited. After intersystem crossing with 100% efficiency, the long-lived state energy of **Zr** or **Hf** is transferred to the UHC, resulting in emission quenching of the metallocene (the efficiency of intermolecular TET was examined by steady-state spectroscopy at low temperature). As a second effect, we reveal, in some cases, the existence of significant coordinative interaction between the title d^0 complexes and monomers and estimate distances at which d^0 metallocene−UHC orbital interactions, responsible for TET and coordination, are effective. These findings provide a new example of TET use for studying intermolecular interactions, in particular, the first example of systematic study of coordination between unsaturated hydrocarbons and d^0 π-complexes by the energy transfer approach.[17]

CHART 1: Molecular Structure of d^0 Metallocenes Zr and Hf as Energy Donors and Unsaturated Hydrocarbons as Triplet Energy Acceptors Employed



2. Experimental Methods

Materials. Methylcyclohexane, toluene, 3-methylpentane, and all unsaturated hydrocarbons of commercial origin (Aldrich, Acros Organics, Lancaster, etc.) were additionally purified, at least, by multiple distillations in high-purity Ar atmosphere, rigorously dried by reflux over lithium aluminum hydride or calcium hydride followed by distillation, and degassed through several freeze−pump−thaw cycles (purity was checked by monitoring the UV−vis absorption and luminescence at 77 K and room temperature (RT)). Norbornylene was distilled several times, dried via reflux over calcium hydride, and sublimed in vacuo through a column filled with activated carbon prior to use. Methylcyclopentadiene and cyclopentadiene were obtained from the respective dimers (Aldrich) by distillation, rigorously dried over calcium hydride, and transferred in vacuo to a quartz cell or a Schlenk flask immediately prior to measurements. Samples of the complexes were prepurified by either recrystallization from stock solutions or vacuum sublimation of the individual complexes at moderate temperatures. The low content of the complexes in the samples was used ($c < 10^{-4}$ mol L^{-1}) to avoid concentration effects at low-temperature experiments.

Instrumentation. 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 an all-glass vacuum line fitted with high-vacuum Teflon stopcocks.

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. Measurements were performed in 1-cm quartz cells at 20 °C and in thin quartz ampules. In all of the experimental cases studied, low-temperature (77 K), rigid glass spectroscopy was used. Low-temperature spectra were obtained with the use of an optical Dewar sample holder. The samples were excited at wavelengths of 300−320 nm; experiments were multiply reproduced due to difficulties with obtaining glassy samples (at high UHC concentrations) suitable for the quantum yield determination. The correction of $\Delta V = 20\%$ due to the contraction in the sample volume upon cooling from RT to 77

K was taken into account for accurate determination of the triplet acceptor concentration. Relative emission efficiencies were measured from the peak areas of the emission spectra. Φ_{LUM} values may reflect an experimental error of 5−10%. All samples were spectroscopically tested for photochemical stability: the metallocenes dissolved in hydrocarbon solvents and unsaturated hydrocarbons were photochemically stable in the time scale of luminescence recording and much longer at room temperature. An important point to emphasize is that the target systems are not amenable to photoreactions in rigid media at cryogenic temperature.

3. Results and Discussion

Properties of Highly Emissive LMCT States Based on Cp_2MCl_2 and Their Nonradiative Deactivation upon Addition of Alkenes and Dienes. Optical Properties. Ti, Zr, and Hf in their 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 (this is mainly referred to Zr- and Hf-based compounds). The low molar absorption coefficients of the first LMCT absorption band (the HOMO-to-LUMO transition), e.g., for Cp_2MCl_2, $\epsilon \approx 200$ mol^{-1} L cm^{-1} for Ti, 950 mol^{-1} L cm^{-1} for Zr, and 1200 mol^{-1} L cm^{-1} for Hf,[4i,16] are indicative of the spin-forbidden nature of the coupled radiative transition to S_0 state. The emission of Cp_2MCl_2 shows a weakly resolved vibronic structure at 77 K and, we presently note, does not change in dissolved ($10^{-6}-10^{-5}$ mol L^{-1}) glassy solutions, which excludes an excimer origin. The values for the radiative lifetimes τ_0 of the long-lived excited states in Cp_2MCl_2 are ca. 9.0 (Ti), 2.0 (Zr), and 0.3 ms (Hf), respectively. In preceding communications,[4i,16] we have hypothesized the emission to be a spin-forbidden radiative transition from a triplet excited state to a singlet ground state: $T_1 \rightarrow S_0$ (phosphorescence). In fact, this corresponds to the values of the rate constant for radiative deactivation, k_r: ca. 100 (Ti), 500 (Zr), and 3300 s^{-1} (Hf), which are approximately 5−7 orders of magnitude smaller compared to the fully allowed singlet−singlet transitions having radiative decay rates of 10^8-10^9 s^{-1}.[3a] The energy difference between the absorption and emission maxima (Stokes shift) in **Zr** and **Hf** up to 1 eV[16] also supports the hypothesis of the triplet origin of the excited states based on Cp_2MCl_2. In the present study, we derive convincing direct photophysical justification for the multiplicity of these highly emissive, long-lived states based on group 4 metallocenes and estimate the dependence of TET on the structure of triplet acceptors used. All experiments were conducted in nonpolar rigid (optically transparent, glassy) solutions made of methylcyclohexane (MCH) and different amounts of UHC at 77 K to rule out a possible dynamic quenching component as well as an exciplex formation under such conditions.

Energy Transfer. It is well-known that efficient quenching of electronically excited states takes place by either energy or electron transfer. For our systems, we rule out the possibility of either reductive or oxidative electron-transfer quenching of Cp_2MCl_2-based excited states. In accordance with a photophysical model and thermodynamically favorable conditions, energy transfer via D*(triplet) + A_o(singlet) → D_o(singlet) + A*(triplet) is effective where $E_{D*(triplet)} > E_{A*(triplet)}$. In fact, this fits our major experimental observations made for group 4 representatives **Zr** and **Hf** as the excited state energy donors (D) and unsaturated hydrocarbons, incorporating one ((a)cyclic alkenes) or two ((a)cyclic dienes) double bonds C=C, as the triplet energy acceptors (A).

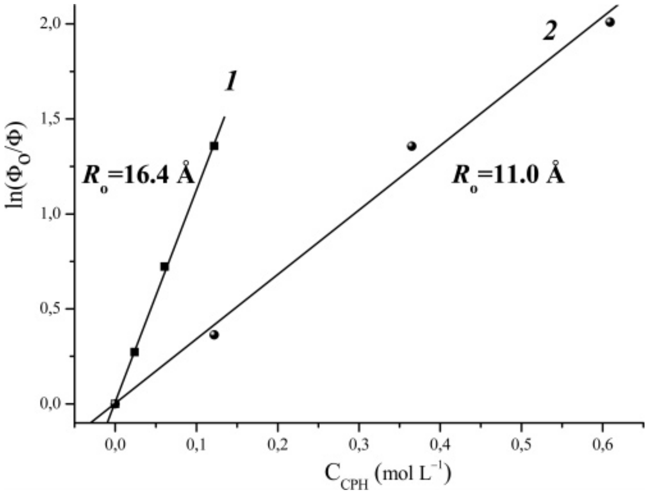
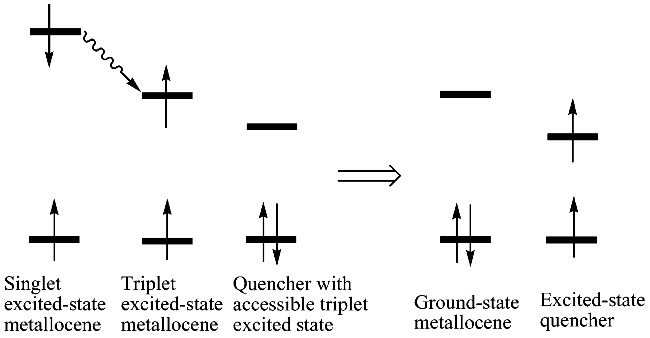


Figure 1. Perrin-type concentration dependence of diphenylamine phosphorescence quenching with cyclopentadiene in glassy solutions of methylcyclohexane (1) and 96% ethanol (2) at 77 K.

SCHEME 1: Bimolecular Energy Transfer via Triplet−Triplet Route



In this regard, it is important that UHCs act as "low-lying energy traps" since they have low-energy (T_1) and high-energy (S_1) excited states available (the energy gap S_1-T_1 is large)[18] and are not amenable to redox or electron-transfer reactions under our conditions (solid environment, cryogenic temperature). Notably, the excited states of unsaturated hydrocarbons presently remain to be of key photophysical interest and efforts. In our study, it was important to determine E_T for all selected UHC acceptors. Preliminarily, we have conducted a set of energy transfers from phosphorescing aromatic amines (e.g., see Figure 1) to target UHCs in methylcyclohexane and thus, under our study conditions, estimated the T_1 energy: for olefins and nonconjugated dienes, $E_T \sim 25\,000$ cm^{-1}; for cyclopentadiene (C_5H_6, CPH) and methylcyclopentadiene (C_6H_8, MCPH), $E_T < 24\,700$ cm^{-1}. In our preceding paper,[16] we estimated E_{00} for Cp_2MCl_2 (dissolved in 3-methylheptane): 24 300 cm^{-1} for **Zr** and 26 300 cm^{-1} for **Hf**. Additionally, it should be noted that there is a drastic increase of the T_1 state upon warming of all solid and liquid metallocene samples to room temperature (E_{00} shifts toward higher energies for up to 1500 cm^{-1}).[19] Therefore, to a first approximation, the thermodynamic requirement $E_{D*} \geq E_{A*(triplet)}$ is met. Thus, with the use of Cp_2MCl_2, d^0 organometallic π-molecules are tested for populating the triplet state of olefins and dienes and, accordingly, the luminescence from d^0 π-complexes is partially or completely quenched via triplet energy transfer (Scheme 1). It is also revealed that the quenching interaction between UHC molecules and the metallocene donor in glassy solutions depends in some way on the size and structure of the UHC and is sought to be proportional to the coupling between the T_1 states of the donor and acceptor.

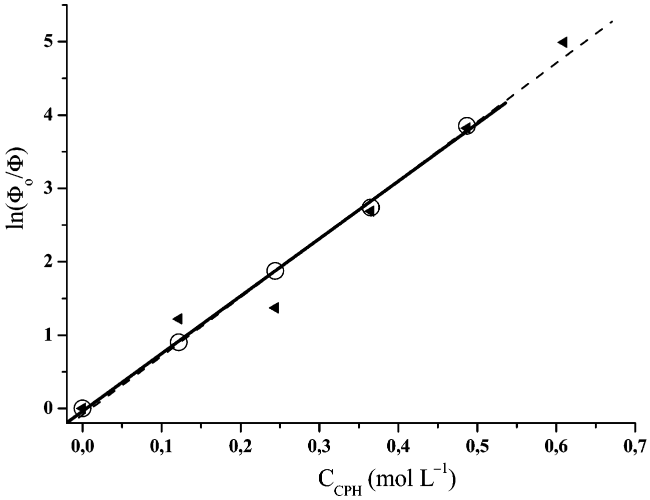


Figure 2. Linear fit of the logarithmic dependence of efficiencies of **Zr** (open circles) and **Hf** (filled triangles) emission quenching on concentration of the triplet quencher (cyclopentadiene) in glassy methylcyclohexane at 77 K.

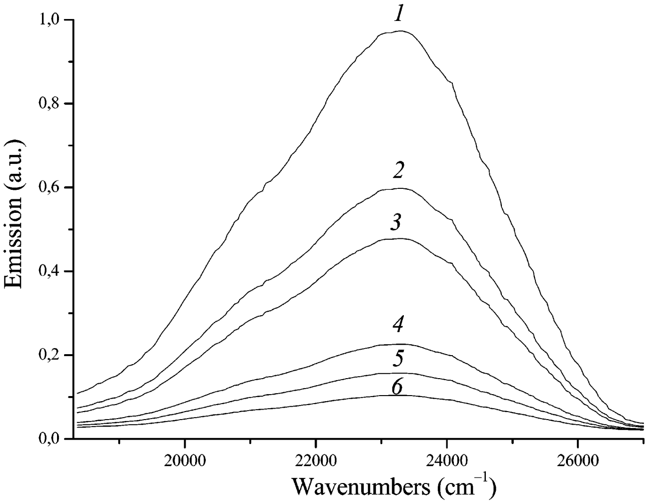


Figure 3. Emission spectra of **Hf** in the absence (1) and presence of various volume concentrations of the triplet energy acceptor (hexene-1) in methylcyclohexane glasses at 77 K. Contents of the alkene added: 10 (2), 20 (3), 30 (4), 40 (5), and 50 vol % (6).

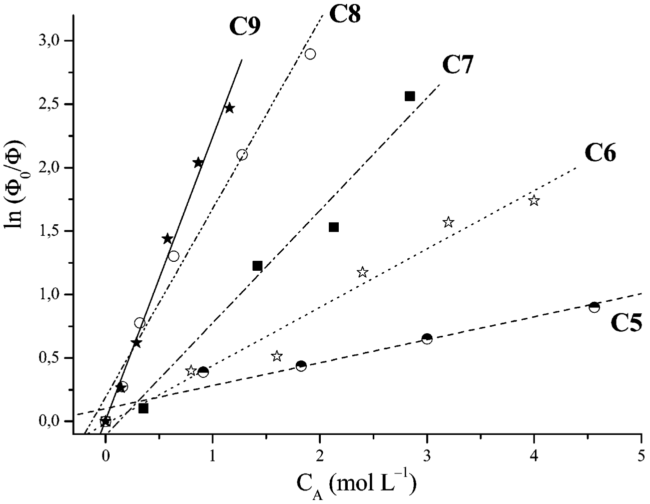


Figure 4. Perrin-type concentration dependences of the hafnocene emission quenching efficiency by nonphosphorescent linear α-olefins (from C_5H_{10} to C_9H_{18}) via energy transfer in methylcyclohexane glasses at 77 K.

Complexation between Sc Complexes and Aromatics. We note in passing that emission quenching of d^0 metallocenes has been reported for group 3 π-complexes ($Cp^*{}_2ScCl$ where $Cp^* = C_5Me_5$) with the use of various aromatic compounds as the energy acceptors; however, no relationship with the energy of T_1 states of the quenchers was reported.[5e] It should be emphasized that, for all aromatic acceptors employed, the emissive state of model $Cp^*{}_2ScCl$ has lower energy than those of the acceptors (e.g., toluene): $E_{A^*(\text{triplet})} \geq E_{D^*(\text{triplet})}$. Nevertheless, quenching of the emissive LMCT state based on the scandocene was observed. This was attributed to the formation of *nonluminescent complexes* of the general formula [D−A] between $Cp^*{}_2ScCl$ and the aromatic quenchers, possessing higher-lying triplet states. No triplet energy transfer occurred in that case. In the present work, for a proper comparison, toluene is also employed as the high-energy triplet trap: no quenching is achieved for the LMCT states based on group 4 analogues **Zr** and **Hf**, which is in line with TET.

Perrin-Type Concentration Dependences of LMCT Emission Quenching in the Presence of Olefins and Dienes as Low-Lying Triplet Energy Traps. The mechanism for triplet energy transfer is usually described by the Dexter electron exchange interaction suggesting D−A orbital overlap and exponential decrease of the ET efficiency with increasing D−A distance.[7a−c] However, both Dexter and Förster (dipole−dipole exchange)[7d] energy transfers strongly depend on the distance between donor and acceptor, and without further experimental data it is not possible to distinguish between these two mechanisms. Notably, triplet energy transfer in a rigid matrix via the Dexter mechanism can be well described by the Perrin model, which assumes an emission quenching relationship, viz., $\Phi_0/\Phi = \exp(NV[A])$ (Φ_0 and Φ are the quantum yield of the donor emission without and in the presence of the triplet-energy acceptor, respectively; $N = 6.02 \times 10^{20}$; $V = (4/3)\pi R^3$ (cm^3), where R is the effective radius of the D−A quenching sphere of the volume V; and [A] is the concentration of the energy acceptor).[20] To resolve this issue, concentration dependences of the metallocene emission quenching were used to rationalize the energy transfer mechanism. Importantly, the Perrin-type concentration dependences are obtained in two-component glassy solutions made of MCH and various UHCs used in this study (with the exceptions of toluene and 3,3-dimethylbutene-1 (DMB)): cyclopentadiene (CPH) (Figure 2), methylcyclopentadiene (MCPH), (*R*)-(+)-limonene (L), cyclohexene (CH), norbornylene (NB), terminal linear olefins (**C5−C9**) (Figures 3−5), 1,7-octadiene (OD), and 1,5-cyclooctadiene (COD). Our experimental data (also given in the Supporting Information) suggest that energy transfers between metallocenes **Hf** (largely) and **Zr** and the monomers occur at radii close to the diameters of interacting molecules (this is detailed hereinafter). Accordingly, for **Hf** as the energy donor, it is established that efficient intercomponent energy transfer takes place in the presence of employed UHCs (with the exception of DMB) and, assuming that the quenching is proportional to the concentration of the UHCs, the electron-exchange resonant mechanism of interaction operates in a solid matrix.

Transition Metal Effect for the Isostructural Donors Zr and Hf: Comparison of Emission Quenching in the Systems [Cp_2MCl_2 + Diene + MCH]. Isostructural origin of molecules generally enables direct insight into ground and excited state properties as well their proper comparison. We wish to report the dependence of emission quenching efficiency on a triplet quencher concentration in dilute glassy solutions obtained for the closely related donors **Zr** and **Hf**. Thus, irradiation of **Zr**

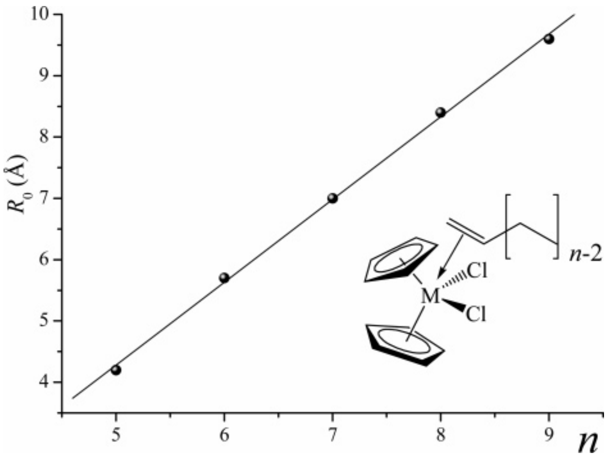


Figure 5. Linear dependence of values of the critical radius for TET from **Hf** on the number of carbon atoms in linear terminal alkenes used as the triplet energy acceptors having $E_T \sim 25\,000$ cm^{-1} (determined in glassy methylcyclohexane as a nonspecific solvent at 77 K).

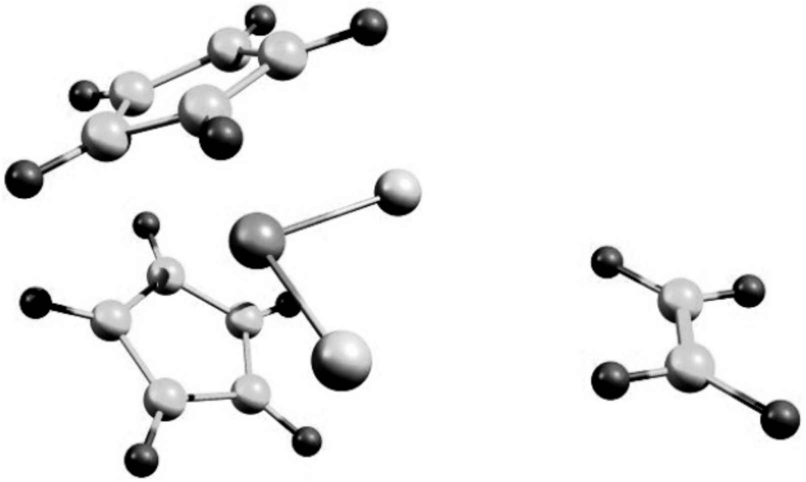
and **Hf** dissolved in MCH with varying small amounts of either cyclopentadiene ([CPH] up to 5−7 vol %) or methylcyclopentadiene ([MCPH] up to 1−2 vol %) leads to complete transfer of the metallocene excitation to the diene. The emission quenching in the representative systems [(**Zr** or **Hf**) + CPH + MCH] rigorously obeys the Perrin equation. Figure 2 demonstrates two linear plots of ln(Φ_0/Φ) against [CPH] for the key samples [**Zr** + CPH + MCH] and [**Hf** + CPH + MCH], where the derived values of *NV* equal 7.8 and those of the D−A critical radius for TET are ca. 14.6 Å. It is intriguing that virtually the same data are obtained for both emitters. Namely, in representatives **Zr** and **Hf**, possessing almost identical structures, the dihedral angles Cp−M−Cp′ between the Cp centroids and the metal ion are close, **Zr** (126.7°) ≅ **Hf** (127.1°),[21] and the radii of the Zr^{4+} and Hf^{4+} ions are essentially the same, 0.82 Å.[22] Meanwhile, it would be reasonable to expect the chemical and photophysical properties of analogous molecules, based on Zr^{4+} and Hf^{4+} ions, to differ owing to the much larger spin−orbit coupling and inclination toward extra-ligand coordination for Hf^{4+} (5d element: [Xe]$4f^{14}5d^0$ electronic configuration in the oxidation state "4+") compared to Zr^{4+} (4d element: [Kr]$4d^0$ electronic configuration in the oxidation state "4+"). In fact, we consider that the greater spin−orbit coupling of Hf is responsible for ca. 7 times decrease of the radiative lifetime τ_0 in **Hf** compared to **Zr** at 77 K. Accordingly, the HOMO−LUMO gap in **Hf** is greater than in **Zr** (e.g., $\Delta E_{\mathrm{LMCT}} = 0.3$ eV and $\Delta E_{00} = 0.15$ eV),[4i] as revealed by associated electrochemical and photophysical studies.[4i,15] In view of the catalytic performance, e.g., the polymerization behavior of hafnocene-based systems is typically different from that of zirconocene analogues.[9]

Similar emission quenching results are obtained with MCPH as the acceptor, although values of the critical radius for TET to MCPH are ca. 1.5 times larger ($R_0 \sim 23$ Å) than in the case of acceptor CPH under other equal factors. Therefore, in view of the Dexter mechanism, the critical radii obtained for energy transfer from **Zr** and **Hf** to MCPH seem to be overestimated (ET via electron-exchange resonant mechanism becomes ineffective as the D−A distance increases beyond ca. 15 Å).[3a] We suggest that these values of R_0 are effective (apparent) and largely reflect chemical (coordinative) interaction between the energy donor (**Zr** or **Hf**) and acceptor molecules (conjugated dienes CPH and, to a greater extent, MCPH), especially in a nonpolar and noncoordinating solvent, such as methylcyclohexane. Correspondingly, the introduction of Me substituent to CPH results in the increase of electronic density in the π-system of two conjugated C═C bonds; therefore, the electron-donating ability of the π-electronic system of the diene increases. Because a diene can act as a relatively weak π-donor ligand with respect to d^0 metal ions and other species (e.g., aromatic Cp^- ligands here), enhancement of the π-electronic donating ability can result in strengthening the [D−A] coordinative interaction (outer-sphere coordination is more probable due to steric reasons), which is reflected in the pronounced enhancement of R_0.

Chain-Length Dependence Test: Unexpected Linear Dependence of the Critical Radius for TET on a Number of Carbon Atoms in Linear α-Olefins. Establishing the basis of the profound influence the UHC nature (geometry, number of C atoms, position of the C═C double bond, etc.) has on the efficiency of emission quenching via triplet energy transfer requires systematic study involving the energy acceptor and donor structural variations. As a first step in this direction, we conducted experiments in glassy solutions made of MCH and UHCs with linear hydrocarbon chains headed by the C═C unsaturated moiety, from pentene-1 to nonene-1. (Unfortunately, linear olefins with longer chains, e.g., decene-1, produced no appropriate glasses at 77 K. On the other hand, alkenes with shorter chains are gaseous and cannot be quantitatively treated with regard to concentration dependences.) Notably, linear terminal alkenes are particularly attractive since they may be treated as substrates for catalytic polymerization as well as the oligomerization products. It is worth nothing that linear α-olefins such as **C6** and **C8** are used, among other applications, as comonomers in the fabrication of linear low-density polyethylene.

The five olefin homologues are sufficient to demonstrate a trend. The experimental values of the D−A critical radius R_0, derived from Perrin-type concentration dependences for **Hf** as the energy donor, grow in the sequence of unhindered α-olefin quenchers: 4.2 Å (for **C5**), 5.7 Å (for **C6**), 7.0 Å (for **C7**), 8.4 Å (for **C8**), and 9.6 Å (for **C9**). This and the above TET experiments and considerations undoubtedly suggest a triplet nature of the emissive LMCT excited states. It is important that α-olefins possess almost equal energies of T_1 state.[18] Therefore, the observed difference in values of the critical radius for TET, under other similar conditions, should be attributed to the structural change (length increase) of a linear olefin. Remarkably, the critical radius for energy transfer increases ca. 1.35 Å with alkene chain growth for every $-CH_2-$ fragment. With the use of systems [**Hf** + C_nH_{2n} (**C5**−**C9**) + MCH], a linear relation, viz., R_0 (Å) = −2.47 + 1.35*n* (Figure 5), is for the first time obtained for ET quenching in systems, incorporating π-complexes and unsaturated hydrocarbons. These observations are anticipated for pronounced chemical interaction between d^0 metallocenes and olefins, principally through inner-sphere donor−acceptor coordination of an olefin chain to a d^0 metal ion (Hf^{4+} here) via in situ formation of labile π-complexes of the general formula [**Hf**−C_nH_{2n}] (Scheme 2). Hence, reducing C═C bond order within the coordinated UHC molecule, to a greater or lesser extent, and η^2-coordination mode are expected to occur. An olefin molecule, as a neutral extra-ligand, is tentatively suggested to enter a d^0 metallocene from the side; although coordination to the central position between the σ-ligands cannot be ruled out (the side coordination can be preferable under kinetic control). The linear dependence R_0 (Å) = −2.47 + 1.35*n* reveals "freezing out" of a fast dynamic process: coordination and labilization of an olefin by a d^0 metallocene. (In fact, thermodynamic equilibrium of the com-

SCHEME 2: Qualitative Representation for Coordinative Interaction of a d^0 Bent Metallocene with Ethylene



plexation may be crucial in the liquid phase at RT; this equilibrium can shift toward the formation of donor−acceptor complexes in a frozen matrix at 77 K.) Accordingly, we arrive at the conclusion that coordinating ability is crucial and noticeable coordinative interaction may be prevented by steric hindrance of either an intervening monomer or aromatic ligands of a d^0 metal complex, or both. These findings are of importance and particular relevance to catalytic reactions (in particular, to an associative mechanism for catalytic polymerization). An analogous associative complex formed by a metallocene and an olefin as a neutral weak π-ligand, bound to d^0 metal ion, has been suggested in a recent NMR study of olefin insertion by zirconocene and hafnocene hydrides via rapid, reversible olefin binding with rate-determining insertion into the M−H bond.[12a] The trend obtained from a systematic alkene chain-length variation provides valuable insight into the behavior of substrates for the Ziegler−Natta and other systems for catalytic polymerization: unsaturated hydrocarbons. We believe that further development of this experimental approach, e.g., a chain-length-dependence test, will be useful for studying conformation in solution, packing in the solid state, specific intermolecular and supramolecular interactions, and so on.

Energy-Transfer Hf Emission Quenching with Bulkier Alkenes (CH, NB) and Nonconjugated Dienes (L, OD) in MCH Glasses. On the basis of low-temperature emission quenching experiments, we are able to estimate the influence of the triplet acceptor structure on energy-transfer efficiency from **Hf**. Although the derived values of the critical radius are close to those of the diameter of interacting molecules, the experiments reveal the influence of the alkene and diene sterics on TET effectiveness. Perhaps not surprising is the observed increase in the critical radius of the emission quenching sphere for more hindered unsaturated energy acceptors (especially for alkene NB where $R_0 \sim 11$ Å), which we attribute to reduced ability to coordinate to the metal ion in **Hf**. Almost identical values of R_0 are obtained for the related energy acceptors CH and L, likely reflecting close steric factors for the D−A orbital interaction: 9.0 Å for CH and 8.8 ± 0.2 Å (for L; due to problems with fine purification and production of optically transparent glasses, we obtained the largest R_0 deviation in the UHC series, as indicated). It is interesting that for diene OD having two nonconjugated terminal C═C fragments bridged by a hexenylene moiety, the critical radius of the D−A quenching sphere is 7.8 Å, which appears to be a mean value between those obtained for α-olefins **C7** and **C8**: 7.0 Å for heptene-1 and 8.4 Å for octene-1. These experimental data are in line with our hypothesis on inner-sphere coordination of the monomer molecule(s): the first C═C double bond coordinates to the metal ion (Hf^{4+} here) and the second distant C═C group of 1,7-octadiene (OD) participates in "physical" quenching. In view of the suggested "complicated" TET mechanism, for acceptor **C8** having the same number of C atoms in a chain compared to OD, the TET radius is enhanced (approximately for half the carbon−carbon bond length) since "physical" quenching is achieved with another **C8** molecule from a second coordination shell of **Hf**.

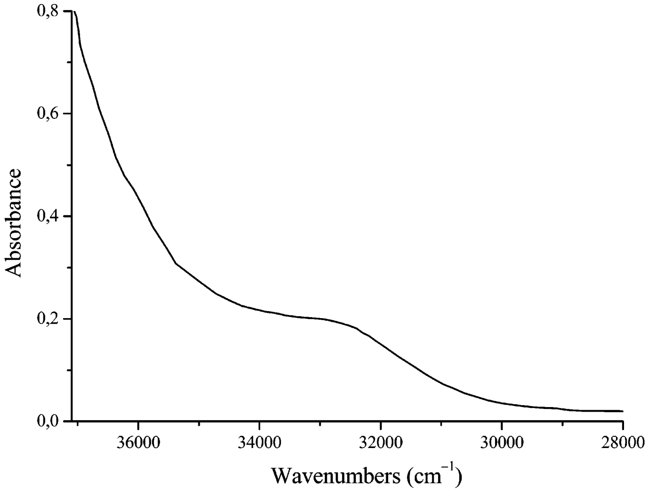


Figure 6. UV-absorption spectrum of **Hf** dissolved in the mixture of methylcyclohexane with norbornylene (1:1 v:v) recorded in a 1-cm quartz cell at room temperature.

Evidence for Pronounced Coordinative Interaction between the Energy Donors and Hydrocarbon Quenchers "Breaking" the Energy Transfer Rule and Thus Yielding Emission Preservation. Unexpected findings are revealed in our emission measurements: pronounced interaction between group 4 precatalysts and UHCs at low concentrations of the former and high concentrations of the latter suggesting low values of the complexation equilibrium constant. Absorption spectra of the metallocenes have very broad, structureless bands and appear to be much less informative (e.g., see a representative absorption spectrum of **Hf** in the mixture of MCH with NB, Figure 6) Now let us consider peculiarities of the quenching process where UHCs, possessing a triplet state close in energy to that of **Zr**, participate. It is intriguing that no direct correlation with the energy of triplet states of the quenchers is observed. There may be some confusion surrounding the quenching

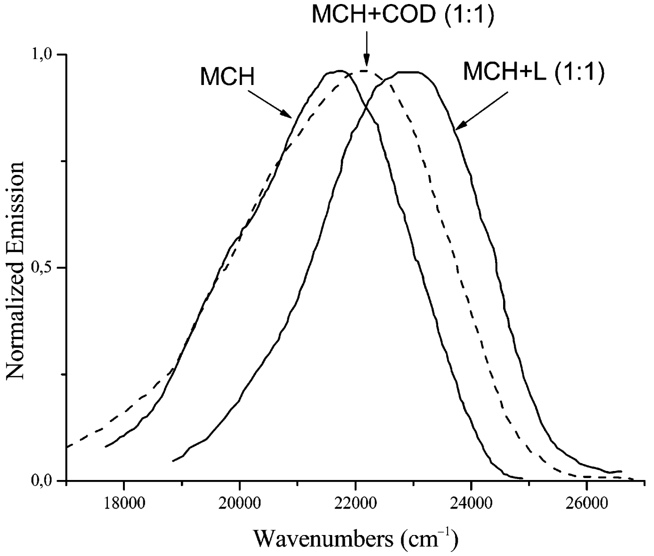


Figure 7. Blue shifts of the emission spectra of **Zr** dissolved in MCH in the presence of (*R*)-(+)-limonene (L, 1:1 v:v) and 1,5-cyclooctadiene (COD, 1:1 v:v; dashed curve) at 77 K.

mechanism, as this was somewhat unexpected. Thus, on one hand, in a number of cases emission spectra (Φ_{LUM}, a curve shape, position of E_{00}, E_{max}, etc.) of the target metallocenes **Zr** and **Hf** remain unchanged in neat glassy (where possible) quenchers. Precisely, an intriguing result is the lack of emission quenching of **Zr** or **Hf** emitting states by triplet trap DMB, having the same in energy low-lying T_1 state as the rest of the alkenes used in this study: $E_T \sim 25\,000$ cm^{-1}. On the other hand, we observed the appearance of significant shifts of emission spectra of **Zr**, as the excitation energy donor, without (or with small) loss in emission quantum efficiency. These results also bear significance in the context of another issue and reveal the presence of the considerable interaction between the excitation energy donor and acceptor molecules. Notably, it may be also the case where triplet states of D and A species are close in energy.

Evidence for the complex formation [D−A] is blue shifts of emission spectra when UHC quenchers of interest (nonconjugated dienes L and COD) added to **Zr** in MCH, as shown in Figures 7 and 8. In addition to the spectral shift, we observe weak (for ca. 15%) quenching of the zirconocene emission at the addition of 50 vol % of diene COD. Because the spectral shift of **Zr** in the presence of diene COD added is less than in that in the presence of diene L and weak emission quenching occurs via TET, it is reasonable to assume that the complex (complexes) [D−A], formed in situ between the starting zirconocene and coordinated COD, possesses (possess) a T_1 state equal (or very close) in energy to that of diene COD. Luminescence quenching occurs via an energy-transfer mechanism by the noncoordinated diene molecules distributed in the vicinity of in situ complexes [**Zr** + *n*diene] (in principle, there is also a possibility for TET quenching by the second C=C bond of the diene, if it is not coordinated).Therefore, the T_1 state energy of noncoordinated quencher COD is equal to 24 900 cm^{-1}. Notably, according to T_1 state energy decrease, the dienes employed in the present work are in the order L > COD > CPH, which also relates to the increased ability of π-electronic systems of C=C groups to interact via a “through-bond” or “through-space” mechanism (Scheme 3).

To provide more evidence for the intermolecular interaction, we conducted experiments with different amounts of the nonconjugated dienes added to donor **Zr**. Thus, addition of UHC L to emitter **Zr**, dissolved in alkane MCH, results in the pronounced nonmonotonic shifts of the emission spectrum up to 1000 cm^{-1} toward higher energies as the diene concentration increases from ca. 5 to 50 vol % and with time (Figures 8 and 9). Notably, in the presence of 0.5−1 vol % L, emission spectra of the system [**Zr** + L + MCH] are practically identical to the starting spectrum of **Zr** in neat MCH. Relatively high concentrations of dienes L and COD, at which pronounced spectral shifts are detected, are rationalized from the point of small values of the complexation equilibrium constant. It should be emphasized that at the addition of UHC to MCH as a solvent, neither the dielectric permittivity ϵ nor the optical dielectric constant n_D^2 (n_D is the index of refraction) appreciably changes: e.g., for neat MCH, $\epsilon = 2.02$ and $n_D = 1.422$; for neat (*R*)-(+)-limonene, $\epsilon = 2.37$ and $n_D = 1.473$. Thus, the observed trend (spectral shift toward higher energies) cannot be assigned to the change in optical and/or dielectric properties of such hydrocarbon media. Accordingly, this is attributed to formation of a (semi-)labile π-complex between molecules of the metallocene precatalyst and unsaturated substrate. We believe that these and similar observations are best explained by coordination of a monomer to a metal center (Zr here). There is much evidence on this regard. To a first approximation, outer-sphere coordination of external, capable of donating electronic density species (e.g., organic molecules) can be modeled as the

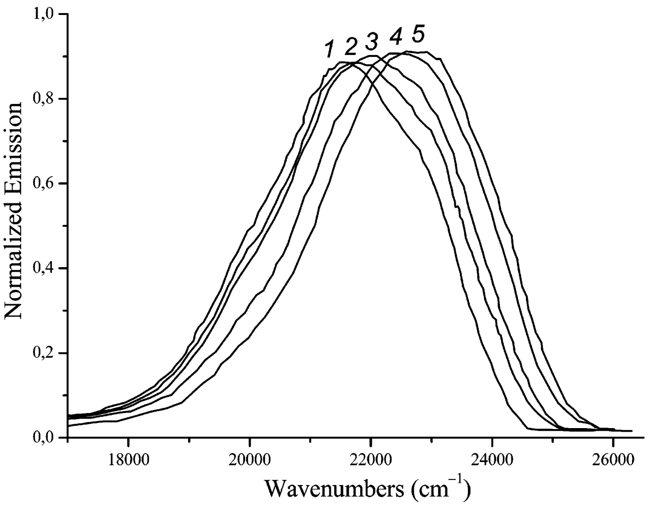
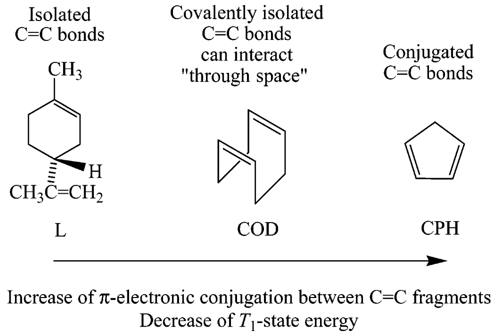


Figure 8. Blue shifts of the emission spectrum of **Zr** in methylcyclohexane at 77 K (1) upon addition of 10 (2), 15 (3), 25 (4), and 50 vol % (5) of (*R*)-(+)-limonene (measured in 2.5 h after addition). The samples were prepared and stored at RT; luminescence spectra were recorded at 77 K.

SCHEME 3: Dienes, Having either Isolated or Interacting π-Electronic Systems of Two C=C Bonds, Resulting in Pronounced Shifts of Low-Temperature Emission Spectra and/or Reduction of Emission Intensity of Zr



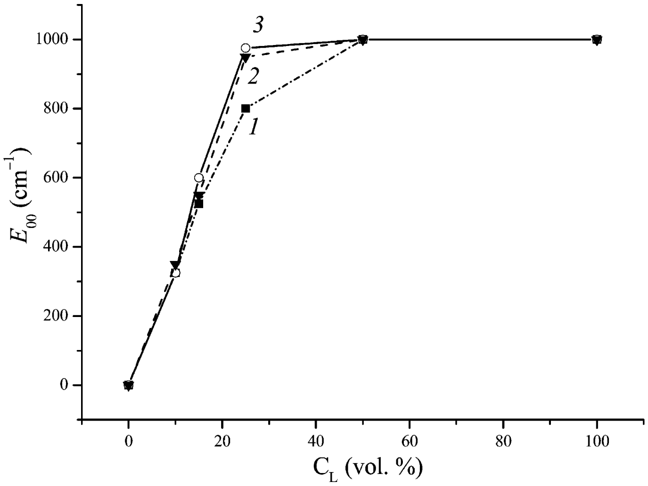


Figure 9. E_{00} energy blue shifts of the emission spectrum of **Zr** dissolved in methylcyclohexane upon addition of coordinating (*R*)-(+)-limonene at 77 K (measured in 2.5 (1), 24 (3), and 48 h (2) after diene addition). The samples were prepared and stored at RT; luminescence spectra were recorded at 77 K.

introduction of more electron-donating moieties to sandwich π-ligands in Cp_2MCl_2, which is possible to do due to ligand additivity, as evidenced earlier[4i] for group 4 metallocenes. According to the associated electrochemical and photophysical study,[4i,15] it was shown that the overall effect of successive introduction of larger sandwich ligands (i.e., better π-donor ligands, e.g., Ind^- and Flu^- compared to Cp^-) and a donor substituent/bridge is enhancement in energy for the HOMO and progressive reduction of the HOMO−LUMO energy gap between the frontier MOs in a d^0 bent metallocene, while the LUMO remains in energy approximately the same (registered as red LMCT spectral shifts, reductions of the electrochemical gap, and decrease of the first oxidation potentials[4i,15]). Importantly, upon principal changes in the inner coordination sphere of d^0 metal ion, a dramatic enhancement in energy for both the LUMO and HOMO−LUMO energy gap in $(\pi\text{-L})_2MX_2$[4a,i] was revealed where the metal-based LUMO is admixed with orbitals of σ-donor ligands, e.g., upon replacement of Cl^- ligands by much stronger Me^- σ-donor ligands, eventually perturbing the LUMO.[4i,15] Moreover, it should be noted that in specific solvents, such as benzene or toluene, forming outer-sphere complexes with metallocenes (which are responsible for relatively high solubility of the π-complexes), metallocene absorption and emission spectra always undergo shifts toward lower energies upon addition or replacement of an alkane solvent (MCH here) for benzene or toluene.

In contrast, the data derived in the present study reveal that the S_0-T_1 gap of metallocene **Zr** is increased in the presence of nonconjugated diene L ($\Delta E_{00} \sim 0.12$ eV) and “partially” (“through-space”) conjugated diene COD ($\Delta E_{00} \sim 0.075$ eV) compared to that of **Zr** in neat MCH (Figure 7). Under such circumstances, one should attribute emission spectral shifts toward a higher energy region for **Zr** to pronounced inner-sphere coordination of dienes L and COD. (This does not rule out the possibility for outer-sphere diene coordination: we suppose that outer-sphere coordination does occur as well.) The T_1 state of **Zr** (the metal-localized LUMO) increases to a greater extent due to electron density donation from the diene to the d^0 metal ion (the coordination probably takes place in a stable η^2-fashion). Observation of such effects in rigid media at 77 K implies that complexation occurs in the ground state.

In summary, we suggest a direct inner-sphere coordination of an unsaturated quencher via a double bond to a d^0 metal center (Zr, Hf) of metallocenes (apparently, still a luminescent complex is formed from a metallocene and UHC quencher(s)). Also, we assume outer-sphere coordination between the π-systems of the aromatic ligands of the complexes and that of unsaturated bonds of hydrocarbon quenchers (e.g., through aromatic π-stacking: approximately parallel face-to-face arrangement). The indicated results imply that, in some cases, if not in all, new luminescent complexes are in situ formed from emitters **Zr** or **Hf** and UHC quenchers. Precatalysts **Zr** and **Hf** are thus coordinated with alkenes and dienes via combination of two or more types of more or less pronounced noncovalent interactions: metal−ligand coordinative bonds, aromatic π-stacking, and other undefined. It is tempting to speculate that such charge transfer or donor−acceptor coordinative interaction reduces the carbon−carbon bond order from 2 to a lesser value in alkenes and dienes; accordingly, in such a case, the T_1 state of the coordinated monomer acceptors should be enhanced. The resulting complexes of the general type $[Cp_2MCl_2{-}n\text{UHC}]$ may be effectively protected from the close contact with unbound UHC molecules, capable of “physical” emission quenching. If so, olefin or diene molecules must be assembled in a very specific way around an emitter, which is isolated and remaining still emissive in such a “cage”. We assume that this is the case of systems incorporating phosphor **Zr** or **Hf** and low-energy triplet acceptor DMB. (This is attributed to steric hindrance introduced by the freely rotating *tert*-butyl group linked with the unsaturated moietyC═C in the α-olefin.) In fact, according to simple molecular modeling, one can assume that bulky DMB is, at least, 4 Å in size; on the other hand, the correlation $R_0 = -2.47 + 1.35n$ predicts that for UHC, having four C atoms in a chain, the critical radius should be ca. 3 Å, which is less than the size of 3,3-dimethylbutene-1. Our energy-transfer experiments show that DMB is indeed ineffective as the quencher not only for emitter **Zr** but also for **Hf**, possessing a higher-lying emissive state.

Simple calculation allows the expectation that the through-space separation of the D−A components exceeds 4 Å, up to 10 Å. More importantly, in a number of cases (e.g., where the quencher is CPH or MCPH possessing two conjugated C═C moieties), efficient quenching of the metallocene luminescence by UHCs occurs within such an assembly. Perhaps, it is much more efficient than that between the donor and acceptor molecules “randomly” distributed in solution bulk. We attribute this to some cooperative (“synergetic”) effect: (i) close approach of the UHC to the metallocene due to its coordination via one C═C bond; (ii) luminescence quenching due to the presence of the energy-accepting moiety—the second C═C bond in the same coordinated UHC molecule. From this point, it is tempting to speculate that triplet-energy-accepting ability, within a UHC series, can vary significantly with their steric requirements. Further research on fundamental aspects of these donor−acceptor interactions is ongoing.

4. Conclusions

This work explores a direct photophysical approach—triplet energy transfer in a rigid, optically transparent matrix—to reveal and systematically study, with the use of polymerization catalysts precursors, group 4 representatives Cp_2MCl_2 (M = Zr and Hf), the triplet nature of rare highly emissive long-lived LMCT excited states, based on d^0 organometallic π-complexes, and their coordinative interaction at low, close to catalytic concentrations (which cannot be achieved with conventional techniques, such as NMR). In the presence of 12 low-lying triplet energy quenchers (alkenes and dienes), emission from the title d^0 metallocenes is quenched in glassy MCH solutions. For the target systems, the energies of the T_1 states of pertinent unsaturated hydrocarbons have been also established via TET. Thus, for organometallic π-complexes, with the use of representatives **Zr** and **Hf** as highly emissive donors and UHCs of the series as the triplet acceptors, it is demonstrated that concentration dependences of the emission quenching efficiency obey the Perrin equation, attributed to the electron-exchange resonant mechanism of interaction. For both phosphors **Zr** and **Hf**, TET occurs in alkaline solutions at the same distances for the same triplet traps (CPH, MCPH), regardless of the difference in spin−orbit coupling of the transition metals. Perhaps the most unexpected result is a relationship between values of the critical radius of quenching sphere, where actual electron-exchange interaction can occur, and the number of carbon atoms in linear α-olefins, viz., R_0 (Å) $= -2.47 + 1.35n$, suggestive of coordinative interaction, in the ground state, between a monomer and a d^0 metal ion in a metallocene. Arrangement of the unsaturated quencher around the d^0 metal core affects the observed TET efficiency and coordinative interaction. Steric hindrance and coordination are proposed to account for the lack of energy-transfer emission quenching with DMB as a low-lying triplet energy trap. Notably, the D and A concentrations are close to those in actual catalytic systems, especially low concentrations of metallocenes ($c \leq 10^{-4}$ mol L^{-1}). The organometallic reactions have proven difficult to study by direct measurements, with evaluation of rate constants being a historical quest. Accordingly, such a photophysical approach may be promising in the mechanistic study of a key stage of organometallic polymerization catalysis: the in situ formation of cationic catalytic species,[9,10] coordination, and following insertion of substrate molecules.

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Supporting Information Available: Concentration dependences for **Hf** and **Zr** emission quenching efficiencies obtained with olefins and dienes employed. This material is available free of charge via the Internet at http://pubs.acs.org.

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