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Radical Mechanisms in the Metallocenes

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Abstract

A special class of sandwich complexes is the metallocenes. The best-known members are the metallocenes of the formula $M(C_5H_5)_2$, where M = zirconium, zinc, titanium, hafnium, vanadium, chromium, molybdenum, tungsten, manganese, iron, ruthenium, osmium, cobalt, rhodium, and nickel. Besides the two cyclopentadienyl rings, the metal can have additional ligands depending on its valence state. These species are also called bis(cyclopentadienyl)metal complexes. Bis(cyclopentadienyl) complexes are called metallocenes or sandwich compounds. Metal-centred radical and cyclopentadienyl radical structures can occur in the metallocene. The anion and cation radicals can also be formed by charge transfer transition.

Keywords: metallocenes, sandwich compound, organometallic compounds, cyclopentadienyl complex, π-complexes, σ-complexes, ionic complexes

1. Introduction

The first metallocene to be classified was ferrocene and was discovered simultaneously in 1951 by Kealy and Pauson; Keally and Pauson were trying to synthesize fulvalene by oxidation of a cyclopentadienyl salt with anhydrous $FeCl_3$. However, instead of this, $C_{10}H_{10}Fe$ is obtained [1]. Miller et al. also reported the same iron product obtained from the reaction of cyclopentadiene with iron in the presence of aluminum, potassium or molybdenum oxides [2]. Wilkinson et al. [3] and Fischer and Pfab [4] studied ferrocene (**Figure 1**) and received the Nobel Prize in 1973 for their work on sandwich compounds. In the bond between the iron atom and the carbon atoms in the cyclopentadienyl (Cp) ligands, each of the carbon atoms contributes equally to the bond. They found that each of the carbon atoms contributed equally to the bond between the carbon atoms in the cyclopentadienyl ligands and the iron atom. In this connection, the effective electrons are the electrons in the d-orbitals of the iron

Figure 1. Ferrocene.

and the π-electrons in the p-orbitals of the Cp ligands. This complex is called ferrocene. This kind of construction was called the metolocene. Co and Ni were used as metals in the first metallocenes. Metallocenes of many elements derived mostly from derivatives used instead of cyclopentadienide have been prepared [5].

2. Classification of metallocenes

A metallocene is a compound typically consisting of two cyclopentadienyl anions (Cp, which is C_5H_5) bound to a metal center (M) in the oxidation state II, with the resulting general formula $(C_5H_5)_2M$. For metalocene derivatives, titanocene dichloride and vanadocene dichloride are the best examples. Some metallocenes and their derivatives exhibit catalytic properties, but metallocenes are seldom used industrially. Cationic group 4 metallocene derivatives are concerned with $[Cp_2ZrCH_3]^+$ catalyze olefin polymerization. Metallocenes are a subset of organometallic compounds called sandwich compounds.

In **Figure 1**, the two parallel structures are cyclopentadienyl anions, which are aromaticly stable and show an ordered arrangement.

Ferrocene, $(C_5H_5)_2Fe$ or Cp_2Fe, is systematically called bis(η^5-cyclopentadienyl)iron(II). Due to the ferrocene name, the first found compound, this type of ferrocene-like structure is called metallocene. IUPAC describes a metallocene as a transition metal between two cyclopentadienyl anions which consist of parallel planes with equal bond lengths and strengths in the sandwich structure. The term "hapticity" means that the equivalent of the five carbon atoms of a cyclopentadienyl ring is completely equivalent. It is pronounced as "pentahapto." It is expressed as η^5. There are exceptions, such as uranocene, in which a uranium atom is sandwiched between two cyclooctatetraene rings.

IUPAC defines the term metalocene as a combination of a d-block metal and a sandwich structure. However, the metallocene term expressed by the sign of the *-ocene* is also applied to compounds such as manganocene or titanocene dichloride (Cp_2TiCl_2) in which the aromatic rings are not parallel or to the i non-transition metal compounds (Cp_2Ba) such as barocene in the chemical literature.

Some metallocene complexes of actinides have been reported to have three cyclopentadienyl ligands for a monometallic complex, and all have been reported to bind η^5 [6].

(η^5-C_5H_5)-metallocene complexes can be classified as shown in **Table 1** [7]. Various (η^5-C_5H_5)-metal complexes are also shown in **Figures 2–4**.

Metallocene complexes can also be classified by type [7]:

(A). Parallel (sandwich)

(B). Half-sandwich

(C). Bent or tilted

(D). Multi-decker [8]

(E). More than two Cp ligands

2.1. Sandwich compound

In organometallic chemistry, a sandwich compound is a chemical compound containing a metal attached to two arene ligands via haptic-covalent bonds. The arenes have the formula $C_nH_{n'}$ substituted derivatives (for example $C_n(CH_3)_n$) and heterocyclic derivatives (for example BC_nH_{n+1}). Since the metal is usually placed between the two rings, it is said to be a "sandwiched." The metallocene is a special sandwich complex class.

Formula	Description
[(η^5-C_5H_5)$_2$M]	Symmetrical, classical "sandwich" structure
[(η^5-C_5H_5)$_2$ML$_x$]	Bent or tilted Cp rings with additional ligands, L
[(η^5-C_5H_5)ML$_x$]	Only one Cp ligand with additional ligands, L ("piano-stool" structure)

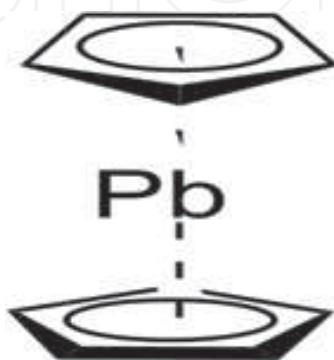**Table 1.** Classification of (η^5-C_5H_5)-metal complexes.

Figure 2. Sandwich or metallocene complexes.

The sandwich compound term entered to the organometallic nomenclature with their studies identifying the structure of ferrocene by X-ray crystallography of Dunitz et al. [9]. The correct structure was proposed several years ago by Robert Burns Woodward and Ernst Otto Fischer separately. The structure helped to explain the unknowns of ferrocene's conformers with an iron atom trapped between two parallel cyclopentadienyl rings. This result showed better the power of X-ray crystallography and accelerated the growth of organometallic chemistry [10]. Ferrocene, a sandwich compound, is shown in **Figure 5**.

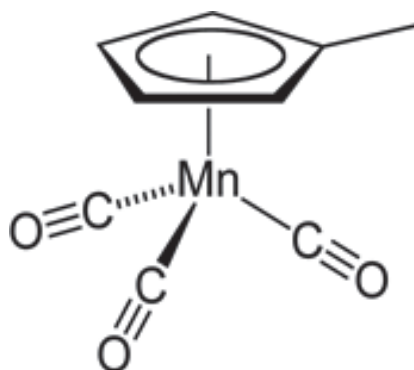**Figure 3.** Bent or tilted metallocenes.

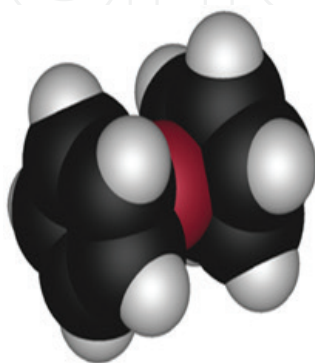**Figure 4.** Half-sandwich complexes ("piano-stool" complexes).

Figure 5. Ferrocene, the archetypal sandwich compound.

The metallocene is generally expressed by the formula $M(C_5H_5)_2$ where M = Cr, Fe, Co, Ni, Pb, Zr, Ru, Rh, Sm, Ti, V, Mo, W, and Zn. Metallosenes are also called bis (cyclopentadienyl) metal complexes.

Apart from the metallocene, the parallel sandwich complexes can be listed as follows. These are not metallocene. However, these are parallel and sandwich compounds.

- **Mixed cyclopentadienyl complexes**: Its general structure is $M(C_5H_5)(C_nH_n)$, such as $Ti(C_5H_5)(C_7H_7)$ and $(C_{60})Fe(C_5H_5Ph_5)$.

- **Bis(benzene)complexes**: Its general structure is $M(C_6H_6)_2$, such as bisbenzene chromium.

- **Bis(cyclooctatetraenyl) complexes**: Its general structure is $M(C_8H_8)_2$, such as $U(C_8H_8)_2$ and $Th(C_8H_8)_2$.

- **Bis(cyclobutadienyl) complexes**: Its general structure is $M(C_4H_4)_2$, such as $Fe(C_4H_4)_2$.

The sandwich compounds can also be formed with inorganic ligands such as $Fe(C_5Me_5)(P_5)$ and $[(P_5)_2Ti]^{2-}$ [11].

2.2. Half-sandwich compounds

It is also called piano-stool compounds. The name of the piano-stool compounds originates from the fact that the structure is likened to a "stool" having a seat with a facial planar organic compounds such as benzene or cyclopentadiene and legs with ligands such as CO or allyl. The metallocenes may have a larger half-sandwich compound family even with a planar organic ligand attached to the surface instead of the two ligands.

2.2.1. Monometallic half-sandwich compounds

These compounds are organometallic. The general structure of the half-sandwich compounds consists of the cyclic polyhapto ligand bound to ML_n, where L is a conjugated ligand [12]. $(C_5H_5)TiCl_3$ and $(C_5H_5)Co(CO)_2$ complexes are among the best examples of this group. Half-sandwich compounds according to the cyclic polyhapto ligand can be examined in two categories: $(\eta^5\text{-}C_5H_5)$ piano stool compounds and $(\eta^6\text{-}C_6H_6)$ piano stool compounds.

(A). $(\eta^5\text{-}C_5H_5)$ piano stool compounds: It contains the cyclopentadienyl ligand, $(\eta^5\text{-}C_5H_5)$, as the cyclic polyhapto ligand of the half-sandwich complex. $(\eta^5\text{-}C_5H_5)V(CO)_4$, $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$, $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_3]$, $(\eta^5\text{-}C_5H_5)V(CO)_4I$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ complexes are among the best examples of this group. $(\eta^5\text{-}C_5H_5)Co(CO)_2$ complex is shown in **Figure 6**.

(B). $(\eta^6\text{-}C_6H_6)$ piano stool compounds: It contains the benzene ring, $(\eta^6\text{-}C_6H_6)$, as the cyclic polyhapto ligand of the half-sandwich complex. The general structure of these compounds consists $(\eta^6\text{-}C_6H_6)ML_3$, where L is typically CO-conjugated ligand and M are metals such as Cr, Mo, W, Mn(I), and Re(I). $(\eta^6\text{-}C_6H_6)$ piano stool complexes are stable compounds with a variety of chemical and material applications and an example of $(\eta^6\text{-}C_6H_6)$ piano stool complex is given in **Figure 7**. The first studies on the $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ compound were carried

out in 1957 and 1958 [13–15]. The crystal structure was determined in 1959 [16]. The subsequent studies came in 1987 and 1989 [17, 18]. The ball-and-stick model of methylcyclopentadienyl manganese tricarbonyl, a "piano stool" compound and CpFe(CO)$_2$I, an example of an unsymmetrical piano stool complex, are shown in **Figures 8** and **9**, respectively.

2.2.2. Dimetallic half-sandwich compounds

Compounds such as the cyclopentadienyliron dicarbonyl dimer and cyclopentadienylmolybdenumtricarbonyl dimer can be considered a special case of half-sandwiches, except that they are dimetallic [17]. A structurally related species is [Ru(C$_6$H$_6$)Cl$_2$]$_2$.

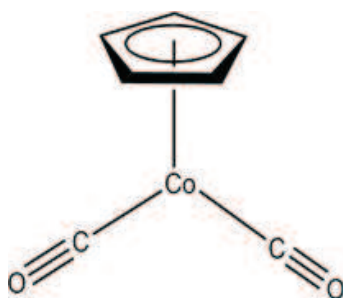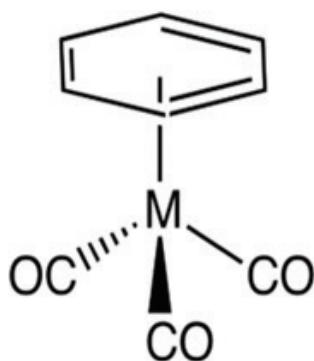**Figure 6.** (η^5-C$_5$H$_5$) piano stool compound.
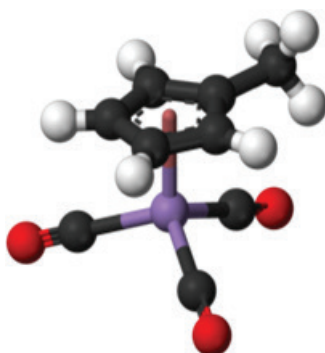

Figure 7. (η^6-C$_6$H$_6$) piano stool compound.

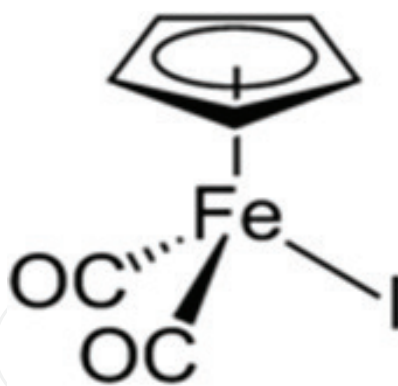**Figure 8.** Ball-and-stick model of methylcyclopentadienyl manganese tricarbonyl, a "piano stool" compound.

Figure 9. $CpFe(CO)_2I$ is an example of an unsymmetrical piano stool complex.

2.3. Bent metallocene

In organometallic chemistry, **bent metallocenes** are a subset of metallocenes. In bent metallocenes, the ring systems coordinated to the metal are not parallel but are tilted at an angle. A common example of a bent metallocene is Cp_2TiCl_2 [19, 20]. Titanocene dicarbonyl, an example of a bent metallocene, is given in **Figure 10**.

Bent metallocene dichlorides of molybdenum and tungsten are also prepared via indirect routes that involve redox at the metal centers.

Bent metallocenes have C_{2v} symmetry. The non-Cp ligands are arrayed in the wedge area. The bent metallocene is represented by the formula Cp_2ML_2. For bent metallocenes, the value of L-M-L angle affects the number of electrons. Molybdocene dichloride (Cp_2MoCl_2) has a Cl-Mo-Cl angle of 82°. In niobosen dichloride, this angle is slightly over 85.6°. For zirconocene dichloride, this angle is greater than 92.1°. This slope indicates that the boundary orbit is directed towards the MCl_2 plane. However, it expresses that the MCl_2 angle does not divide [21].

2.4. Multi-decker sandwich compounds

The dicationic triscyclopentadienyl dinickel complex $[Ni_2Cp_3](BF_4)_2$ was the first multidecker sandwich complex. Since this discovery, many multidecker sandwich compounds have been

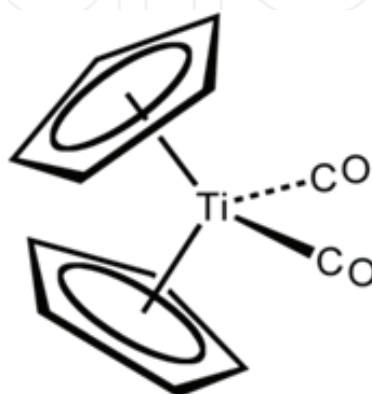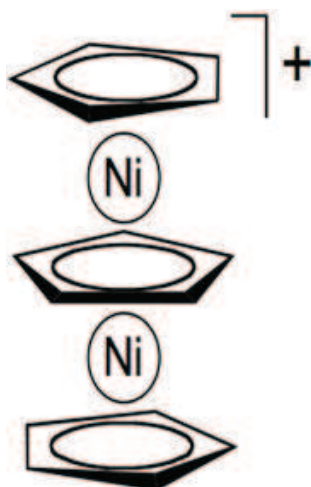**Figure 10.** Titanocene dicarbonyl is an example of a bent metallocene.

Figure 11. $[Ni_2Cp_3]^+$ is an example of triple-decker sandwich complex.

discovered. Especially, the triple deckers are the most important [22]. Different multi-decker sandwich complexes have been obtained by adding Cp^*Ru^+ to preformed sandwich complexes [23].

Triple-decker complexes are composed of three Cp anions and two metal cations in alternating order. The first triple-decker sandwich complex, $[Ni_2Cp_3]^+$, was reported in 1972. $[Ni_2Cp_3]^+$, an example of a triple-decker sandwich complex, is shown in **Figure 11**. Many examples have been reported subsequently, often with boron-containing rings [8].

3. Radical properties of metallocenes

3.1. Cyclopentadienyl radical and metal-substituted cyclopentadienyl radicals

EPR/spin trapping experiments were performed by direct irradiation of benzene solutions of the zirconocenes in the spectrometer cavity. Various spin traps have been used to determine the nature of **the cyclopentadienyl-type radical species**. These spin traps include *N-tert*-butyl-*α*-phenylnitrone (PBN), nitrosodurene (ND), and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) [24, 25]. According to the NIEHS Spin Trap Database [24, 25], the hyperfine coupling constants (*hfcc*) of the spin adducts detected can be attributed to **the cyclopentadienyl type radicals** [26]. Therefore, the primary photochemical act can be described by **Figure 12**.

The presence of radical intermediates in the zirconocenes' photochemical reactions suggests a possible use as photoinitiators for radical polymerisation processes. In order to test the effectiveness of these organometallic photoinitiators, Similar EPR/spin trapping experiments were carried out in the presence of different alkenes such as 1-pentene, methyl methacrylate (MMA) and *tert*-butyl acrylate (*t*BA) and in different solvents such as benzene and dichloromethane. During irradiation of the zirconocene/alkene mixtures, the growth of the EPR signal of **a carbon-centred radical** was detected [26].
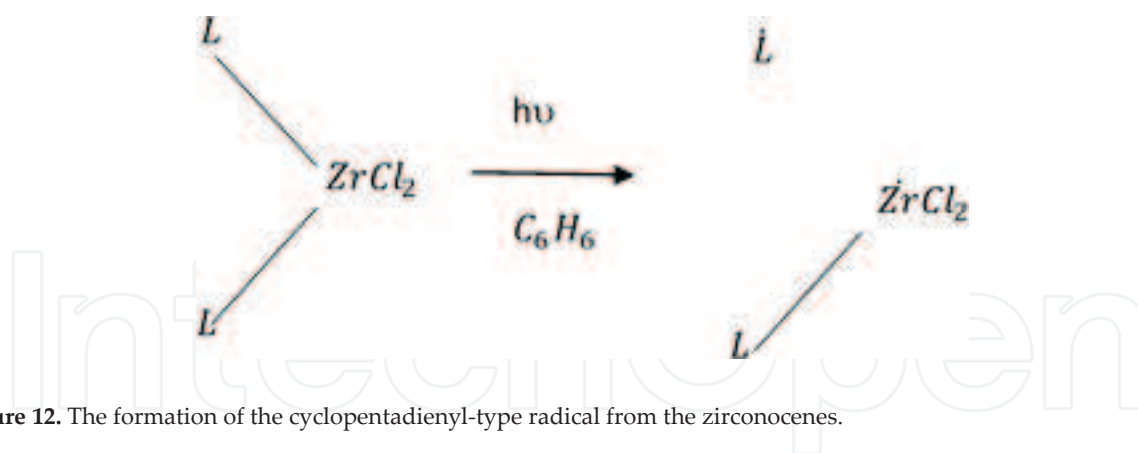
Figure 12. The formation of the cyclopentadienyl-type radical from the zirconocenes.

Due to the resonance state of **the cyclopentadienyl radical**, the bonds to the cyclopentadienyl ring are easily homolized. This situation is discussed in two respects. First, the photolysis is applied to a wide variety of cyclopentadienyl-metallic compounds by ultraviolet light. This effect leads **to the cyclopentadienyl radicals** and **the metal-centered radicals**. Some of these radicals have been characterized by EPR spectroscopy. Second, t-butoxyl radicals react with some other cyclopentadienyl-metallic compounds by removing hydrogen to give **the metal-substituted cyclopentadienyl radicals**.

The general characteristic of many cyclopentadienyl-metallic compounds is that they are not reactive. However, some are quite active. They also exhibit a stability profile for the cyclopentadienyl (5-anulene) ligand, where homolytic reactions are present. This causes the reactions to be homolytic. This has two important consequences. It causes the carbon-metal bond, which is the formation point of **the metal-centered radicals** and **the cyclopentadienyl radicals**, to be light-sensitive. Second, if bimolecular homolytic substitution does not readily occur at the metal center, hydrogen may be abstracted from the ring to give **a metal-substituted cyclopentadienyl radical** [27].

The photosensitivity work of the cyclopentadienyl-metal bond was first applied to tin(IV) derivatives. No significant EPR signal can be detected if simple alkyltin compounds are irradiated in solution with ultraviolet light in an EPR spectrometer cavity. Under the same conditions, cyclopentadienyltin(IV) compounds, η^1-$CpSnL_3$ (,L = Cp, alkyl, aryl, Cl, $MeCO_2$, etc.) give a strong sextet spectrum of cyclopentadienyl radicals [28]; this obscures the spectrum of the radical $\dot{S}nL_3$, but this radical can be identified by virtue of its characteristic reactions with reagents such as alkenes, alkyl halides, and 1,2-diones. For this reason, it is seen that it contains simple unimolecular homolysis. The pentahapto cyclopentadienyltin(II) compounds similarly show the spectrum of the $\dot{C}p$ radical, but an insoluble solid separates, and the fate of the tin moiety is unknown [29]. Similar studies have been carried out on cyclopentadienyl derivatives of other metals. The cyclopentadienyl derivatives of other metals, $CpML_n$, have been subjected to similar works. When M, lithium, mercury, tin(IV), tin(II), lead(IV), lead(II), titanium(IV), or zirconium(IV) are used as metals, M, the spectrum of the cyclopentadienyl radical is obtained. Cyclopentadienyl derivatives of beryllium, magnesium, boron, silicon, and germanium exhibit a very poor spectrum, but, in the presence of di-t-butyl peroxide, the compounds Cp_2Be, $CpBeCl$, Cp_2Mg, and $CpGeCl_3$ give the cyclopentadienyl radical under the effect of an S_H2 reaction in the metal center [30, 31].

When the metal carries both cyclopentadienyl and alkyl (R) groups, cleavage of the Cp—M and R—M bonds may be in competition. Irradiation of alkylcyclopentadienyltin(IV) compounds gives only the cyclopentadienyl radical but cyclopentadienyltriethyl-lead gives $\dot{C}p$ above −50°C and $\dot{E}t$ below −100°C, and both in between [28, 32]. Bis(cyclopentadienyl) zirconium dichloride give a rather weak $\dot{C}p$ spectrum, but Cp_2ZrMe_2 gives only the methyl radical [33].

Cyclopentadienylmethylberyllium reacts with t-butoxyl radicals to show predominantly the spectrum of the cyclopentadienyl radical below −60°C, but at −30°C the concentrations of cyclopentadienyl and methyl radicals are approximately equal [34]. However, with cyclopentadienylmethyl mercury at the normal concentration, the principal species which are observed are $\dot{C}p$ at −75°C, and $\dot{M}e$ at −130°C [35].

The EPR spectra have been studied with the parent cyclopentadienyl radical generated by several routes such as γ-irradiation on both crystalline [36, 37] and liquid cyclopentadiene [38], by pyrolysis of a molecular beam of ferrocene and azobenzene [39] and recently by hydrogen abstraction of cyclopentadiene with the *tert*-butoxy radical in solution [40, 41].

EPR spectroscopy has been used to study the photolysis of the compounds $(C_5H_5)_2ZrCl_2$, $(Me_5C_5)_2ZrCl_2$, $(C_5H_5)_2ZrMe_2$, $(C_5H_5)_2ZrMeCl$ and $(C_5Me_5)_2ZrMe_2$. The cyclopentadienyl radical is formed in the first two compounds, and the methyl radical is formed in the third and fourth compounds. But it can be said that both cyclopentadienyl and methyl radical exist in $(C_5Me_5)_2ZrMe_2$ compound [42].

The experimental and theoretical observations reported above are consistent with the notion that the reactive excited state in the bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2), bis(pentamethyl-cyclopentadienyl)zirconium dichloride ($Cp_2^*ZrCl_2$) and bis(indenyl)zirconium dichloride (Ind_2ZrCl_2) complexes are of the L → Zr (L = Cp, Cp*, Ind) charge transfer type. Such the ligand-to-metal charge-transfer (LMCT) states would lead to formal reduction of the metal and oxidation of the ring system. Consistent with LMCT excitation, these excited states may dissociate, giving rise to free $\dot{L}$ and $L\dot{Z}rCl_2$ radicals. These results are consistent with the earlier reports of photochemistry of zirconium complexes parallel to titanium derivatives for $(C_5H_5)_2ZrCl_2$ [43].

The reaction shown in **Figure 12** is very consistent with the EPR results. In this reaction, the photo-induced cleavage of one of the L—Zr bonds as the primary excited state reaction is generally believed to be the case [44].

3.2. Anion and cation radicals formed in metallocenes

The redox, photophysical, and photochemical properties of the homologous bent metallocenes of group 4 transition metals are emphasized. On the systematic variation of the definition of ligands of metal ions (Ti, Zr, or Hf), auxiliary π- and monodentate σ- (Cl, Me) ligands, a comparative analysis of electron transfer induced transformations and ligand-to-metal charge transfer excited states was carried out for bent metalocene complexes. Linear correlations between optical and redox HOMO-LUMO electron transitions are found for such

organometallic π-complexes. It is proposed that the combination of spectroscopic and electrochemical techniques provide important diagnostics to determine "ionization potential" and "electron affinity" in the solution and the energy gap in metalocene complexes [45].

For the synthesis of dithiolane complexes [Cp(2)M(S(2)C(2)(H)R)] (M = Mo or W; R = phenyl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl or quinoxalin-2-yl) and [Cp(2)Mo(S(2)C(2)(Me) (pyridin-2-yl)] compounds were prepared. These compounds are electrochemically subjected to one-electron reduction and one-electron oxidation process. For a Mo compound, each redox exchange occurs at a more positive potential than the value for a W compound. Monocations of both compounds were produced by chemical and electrochemical oxidation. For [Cp(2)Mo(S(2)C(2)(H)R)](+)/[Cp(2)Mo(S(2)C(2)(H)R)] (R = Ph or pyridin-3-yl) redox pairs, the changes in Mo—S, SC and CC bond lengths of the {MoSCCS} moiety are consistent with the oxidation process involving an electron loss from the π-orbital in Mo—S and C—S antibonding and C—C bonding. When the EPR spectrum of each Mo cation is examined, it is understood that the unpaired electron is weakly bound to the ditiolan proton. According to the results of DFT calculations, the unpaired electrons in the monoanions are localized on the metal, more than mono-cations. Furthermore, according to the EPR spectrum, the hyperfine structure splits of mono anions containing Mo are larger than those of mono cations. The reduction of [Cp(2)W(S(2)C(2)(H)(quinoxalin-2-yl)] takes place at a more positive potential than expected for Mo. The EPR spectrum of the mono-anion is typical for an organic radical. DFT calculations show that these properties are due to the addition of a the electron to quinoxalin-2-yl π-orbital [46].

The cyclic voltammetry of cobaltocene and nickelocene revealed five redox states, from dication to dianion. In situations where it is not possible to work with conventional electrodes at traditional temperatures, operation potential can be extended using low-temperature solvents (SO_2, THF) and ultramicroelectrode techniques. The $Cp_2M^{0/-}$, $Cp_2M^{-/2-}$, and $Cp_2M^{+/2+}$ redox reactions of the previously known $Cp_2M^{0/+}$ redox couples are shown [47].

The classical metalocenes, ferrocene, and ruthenocene are easily soluble in the pure ethyl 2-cyanoacrylate (CA) monomer. The electronic spectra of the resulting solutions show a near-ultraviolet absorption band as a result of the charge-transfer transition to the solvent (metallocene → CA). The one-electron oxidation of the metallocene occurs when this band is exposed to irradiation. The anionic polymerization of the electrophilic monomer begins with the addition of the latter species to CA [48].

A large series of studies have been devoted to metallocenes, starting with the simplest representatives of compounds of this class-ferrocene [49] and its derivatives [50–55]. Comparison of the results of the calculation by the Hückel molecular orbital method with the observed hyperfine structure of EPR spectra [51] yields a quantitative distribution of the spin density in the radical-anion. Overall, the ferrocenyl group is destabilizing compared with the phenyl group. In the presence of both groups in one molecule, the degree of delocalization of the spin density is greater in the direction of the benzene ring [52].

Stable paramagnetic semiquinones of the metallocene series are formed on oxidation of ketones containing the a methylene group [53, 54].

The ease of the one-electron oxidation of metallocene derivatives is confirmed by the formation of paramagnetic salts, where the anionic component may consist of the radical-anion derived from the organic one-electron acceptor tetracyanoquinodimethane (TCNQ) [56]. Such salts are in essence organometallic analogues of charge transfer complexes [57].

Ferrocene and its derivatives turn into cation radicals by the reversible one-electron oxidation. These radicals are called "ferricenium" cations. The iron atom is the center of the cation radical and localized. Conversely, the hole transfers via conjugated systems were proven for bis(ferrocenyl) ethylene cation radical [58] and thebis (fulvaleneiron) cation radical [59]. The unpaired electron is delocalise on both metallocene residues in the bis (fulvaleneiron) cation radical, and Extended Huckel MO calculations [60] support this situation. Alternatively, very rapid intra-ionic intervalence electron transfer can occur between the formal Fe(II) and Fe(III) atoms. In general, the ethylene bonds in the organic cation radicals are weak and the barrier to rotation is significantly reduced relative to the neutral ethylene derivative. This property of the ethylene bond in the cation radicals has been used to investigate many reaction mechanisms [61]. The cation radicals of the ferrocenyl ethylene are not subject to the cis-to-trans isomerization process. The calculations show that the cation radical center is only in the iron atom, not in the ethylene bond [62]. Therefore, one-electron oxidation of ferrocenyl ethylene occurs at the iron atom. For this reason, the stable enol bound to a ferrocene redox center gives a cation radical through an electron oxidation. This species is characterized as a ferricenic salt rather than an enol cation radical [63].

The cationic forms of the metalocene (the metallocinium cations) provide interesting possibilities by forming charge-transfer complexes with various biological macromolecules. Although the suitability of the metallocene compounds has not been discussed yet, Szent-Györgyi emphasized that the charge-transfer interactions of metallocene compounds are of interest to biological problems [64].

The basic coenzymes are all conjugate compounds: DPN, TPN, FAD, FMN, quinones, folic acids, pyridoxal phosphate, etc. The all of the significant coenzymes are all conjugated compounds: DPN, TPN, FAD, FMN, quinones, folic acids, pyridoxal phosphate, etc. Likewise, steroids and a large numbers of pharmacological agents contain suitable conjugate moieties for the charge transfer interactions. The electronic delocalization is thought to be one of their main features [65]. It seemed of interest, therefore, to examine the possible electron-donor properties of some biologically important molecules, particularly of conjugated systems likely to be involved in electron-transfer phenomena in relation to the acceptor characteristics of the metallocenes. The capacity of metallocinium cations to accept π-electrons might, in fact, be employed toward this end. They could serve as probes of the electron-donating characteristics of conjugated biological systems. The ferricinium, the bis-benzene-chromium, and the cobalticinium cations apparently display the required physicochemical properties. All these compounds have aromatic properties. The ferricinium, the bis-benzene-chromium, and the cobalticinium cations contain two parallel conjugated rings, which are either five- or six-membered. They are readily soluble in water. Aqueous solutions of the ferricinium salts [66] and bis-benzene-chromium salts [67] are reasonably stable in the dark.

The cobalticinium salts are exceptionally stable in water [68]. The simple application of a metallic cation between the two aromatic rings has three important consequences for the investigation of biological systems:

(1) The aromatic system becomes more soluble in water.

(2) It becomes a good electron acceptor.

(3) The tightly bound metal ion can be identified by optical, EPR and NMR spectra and is an excellent label of the aromatic system.

The solubility in water of the metallocinium cations has a distinct advantage. Most of the conventional π-acceptors can only be examined in less polar solvents such as chloroform or dimethylformamide [69].

The formation of stable η^5-complexes between fullerenes and transition metals is highly improbable because the conjugated system is rather strongly delocalized, and the polarization of the atoms of the five-member face is weak. There is an opinion that the fullerene structure will change by the addition of R groups, hydrogen (H), methyl (Me), or phenyl (Ph) to the α-position of the same five-membered face, and thus the conjugate system will deteriorate.

The cyclopentadienyl ion obtained from the fullerene plays an important role in the formation of complexes with transition metals [70]. The molecular structure of ferrocene/C_{70}-fullerene hybrid [71] is given in **Figure 13**. There are two obstacles to producing the cyclopentadienyl
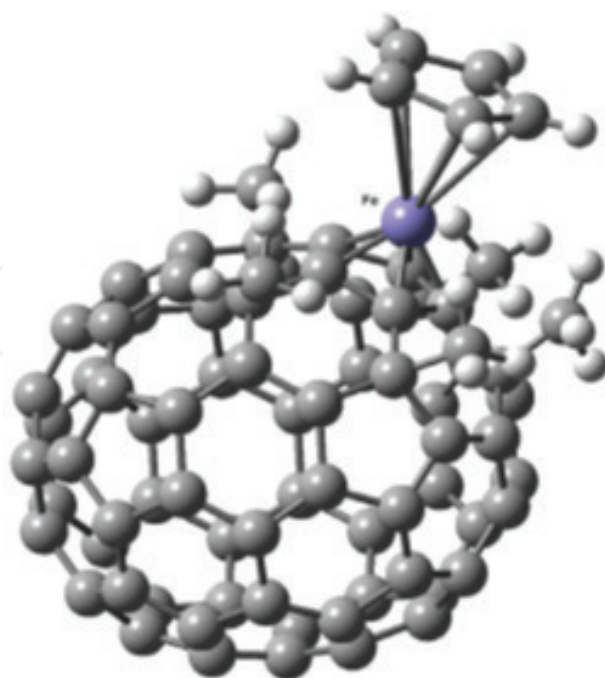

Figure 13. Molecular structure of ferrocene/C_{70}-fullerene hybrid.

ion: first, it is difficult to form a barrier around the cyclopentadienyl ring. And the second is the difficulty in ionizing to produce the cyclopentadienyl group.

The same idea, that is, double-decker ferrocene complexes, has also been examined by the Nakamura group [72, 73]. They studied both theoretical and experimental arguments and found that the addition of a second ferrocene fraction leads to strong instability and can produce very short-lived radical ion pairs [74]. The complex $2\eta^5$-π-$(CpFe)_2$-$C_{60}H_{10}$ [75], double-decker ferrocene complex, is shown in **Figure 14**.

Figure 14. Complex $2\eta^5$-π-$(CpFe)_2$-$C_{60}H_{10}$.

4. Conclusion

In metallocenes, the radicals can occur in a variety of ways. Photolysis (ultraviolet light), radiolysis (gamma-irradiation), spin trapping and photochemical reactions can be created radical. It has been observed that a wide variety of radicals are formed by these methods. The ionic radicals are formed through charge-transfer interactions.

Metallocenes can form a wide variety of radicals. However, the two main types of radical groups gain weight. These are the cyclopentadienyl radicals and the ionic radicals. The cyclopentadienyl radicals are distinguished as the cyclopentadienyl radical and the metal-centered cyclopentadienyl radical.

Other radicals that can occur outside of these radicals can be expressed as follows: the carbon-centred radical, the metal-centred radical, various anion and cation radicals of metallocenes, dianion and dication radicals, and semiquinone radicals of metallocenes.

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