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Photochemistry of *ansa*-zirconocenes: ethylene-bis(1-indenyl)- and ethylene-bis(4,7-dimethyl-1-indenyl) zirconium dichlorides

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Abstract

This paper reports the full details of photochemical experiments on *ansa* ethylene-bis(indenyl) zirconium dichlorides derivatives. Photolysis of the 50 : 50 *meso* : *racemic* isomeric mixtures of ethylene-bis(1-indenyl) zirconium dichloride [EBIZrCl_2] and ethylene-bis(4,7-dimethyl-1-indenyl) zirconium dichlorides [EBDMIZrCl_2] produces a photostationary state made up of *racemic* (60%) and *meso* (40%) isomers. ESR spin trapping experiments showed the photogeneration of ligand- and zirconium-centered radicals. It is proposed that the *meso*-to-*racemic* photoconversion mechanism first involves the cleavage of one of the two metal-indenyl bonds. This generates a biradical species that quickly converts to the more stable products such as the *racemic* isomers of EBIZrCl_2 and EBDMIZrCl_2. The study of the electronic spectra of EBIZrCl_2, EBDMIZrCl_2 and comparison with those of Cp_2ZrCl_2, $Cp^*_2ZrCl_2$ and Ind_2ZrCl_2 showed that the reactive excited states of *ansa*-zirconocenes are associated with LMCT transitions. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Metallocenes; Zirconium complexes; Photolysis; ESR spin trapping

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1. Introduction

Group IV transition metals form stereorigid chiral complexes with *ansa* bis(1-indenyl) ligands [1–3]. These complexes have been used as pre-catalysts in stereospecific polymerization [4–9] and in the asymmetric hydrogenation of olefins [10–12]. They have also been used in various stoichiometric enantioselective transformations [13]. Generally, synthesis of these bridged metallocenes is achieved by reacting a prochiral ligand with the appropriate metal halide [1–3]. This synthesis procedure forms an isomeric mixture of products with varying catalytic activities. Although synthetic strategies aimed at minimizing or eliminating the formation of one of the isomers have been set up, these cannot be generalized. Moreover, the total reaction yield is generally quite low. Therefore, any method of synthesis or purification able to separate the stereoisomers would be of great scientific and technological importance.

Previous studies have shown that for ethylene-bis(4,5,6,7-tetrahydro-1-indenyl) titanium dichloride an efficient *meso*-to-*racemic* conversion can be photoinduced [1–3]. In that case, a combined irradiation/evaporation technique made it possible to convert *meso*/*racemic* mixtures into pure *racemic* isomers. This technique cannot be generalized to other bridged metallocenes, especially when the unwanted isomer is the least soluble. Despite their importance in organometallic chemistry and catalysis few studies have been performed on the photochemistry of *ansa*-metallocene complexes of Ti, Zr and Hf [14–16]. On the other hand also too few photochemical studies of metal (Ti, Zr, Hf) cyclopentadienyl complexes have been conducted to allow any broad generalization to be made except that cleavage of one of the metal-cyclopentadienyl bond can be photoinduced [17–20]. Moreover, while the relationship between Group IV transition metal metallocene structural properties and catalytic activity have been thoroughly studied, very little is known about the relationship between electronic properties and catalytic activity.

This work reports a study of the electronic spectra and photochemical behavior of some zirconium metallocenes: in particular the *meso* and *racemic* isomers and *meso*/*racemic* mixtures of ethylene-bis(η^5-1-indenyl) zirconium dichloride (EBIZrCl_2, **4**) and ethylene-bis(η^5-4,7-dimethyl-1-indenyl) zirconium dichloride (EBDMIZrCl_2, **5**). In addition their photochemical behavior is compared with that of other similar compounds with unbridged ligands such as bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2,

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1), bis(pentamethyl-cyclopentadienyl) zirconium dichloride ($Cp_2{}^*ZrCl_2$, **2**) and bis(indenyl) zirconium dichloride (Ind_2ZrCl_2, **3**).

2. Experimental details

2.1. Spectra

All UV–Vis absorption spectra were obtained using a Jasco UVIDEC-650 double beam spectrophotometer. All NMR data were acquired using a Bruker spectrometer operating at 200,13 MHz for ^1H in the Fourier transform mode. All NMR solvents were dried over $LiAlH_4$ and distilled before use.

ESR spectra were obtained using a Bruker ER 200D spectrometer operating in the X-band. Field calibrations were made on the basis of the hyperfine splitting of di t-butylnitroxide generated in situ by photolysis in benzene ($a_N = 15.404$ G) [21].

2.2. Materials

C_6H_6, $CDCl_3$ and CCl_4 solvents were purchased from Fluka or Aldrich as spectroscopic grade and distilled under argon on sodium/benzophenone prior to use. The spin traps 2-methyl-2-nitropropane (MNO_2P) and N-*tert*-butyl-α-phenylnitrone (PBN) were used as received from Aldrich. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Sigma and distilled under vacuum. Nitrosodurene (2,3,5,6-tetramethylnitrososobenzene, ND) was prepared as described in the literature [22,23]. Cp_2ZrCl_2, $Cp_2{}^*ZrCl_2$, Ind_2ZrCl_2 were obtained from Strem Chemical and purified according to the method in the literature [24]. 50 : 50 mixture of the *racemic* and *meso* complexes of $EBIZrCl_2$ and $EBDMIZrCl_2$ and their pure isomers were prepared as reported in the literature [25,26].

2.3. Photochemical procedures

UV-photolysis was performed with light from a 500 W Oriel Hg lamp housing the apparatus set on an optical rail. Monochromatic light was obtained using an Applied Photophysics *f*/3.4 monochromator or with bandpass interference filters from Ealing or Oriel Corp.

2.3.1. Photolysis of zirconocene dichloride complexes

Selective photolysis was carried out by irradiation of each of the complexes at 366 nm, corresponding to LMCT transition of complexes **1-3**. Selective photolysis of the *ansa* metallocenes **4** and **5** was performed using the following wavelengths: 366 nm for the 50 : 50 mixtures of the *meso* and *racemic* isomers, 436 nm for the pure *racemic* isomers **4r** and **5r**. The spectral changes accompanying irradiation of *ansa* zirconocene complexes were monitored in the UV–Vis and, in all cases, corresponded to the consumption of the *meso* complexes **4m** and **5m** and the generation of the corresponding **4r** and **5r** isomers. The opposite held true for the **4r** and **5r** photoisomerization.

The photostationary state composition (**4m** : **4r** and **5m** : **5r** ca. 40 : 60 in C_6H_6) was determined by measuring the change in molar absorptivities of *meso* and *racemic* isomers associated with their respective absorption maxima.

2.3.2. Photochemical experiments in the NMR tube

A typical analytical photolysis was carried out as follows: an NMR tube with a vacuum line adapter was charged with 4.5 mg of **4m** : **4r** isomers in C_6D_6 (0.5 ml). After the tube was capped, it was immersed in a water-filled quartz Dewar in front of the focused photolysis beam. In some cases the reaction was monitored periodically by examining the recognizable groups of signals in the NMR spectrum of complexes **4m** and **4r**. In other cases the analysis was performed after irradiation for 1 h. After irradiation, the reaction mixture was take back up into the vacuum line to remove the solvent. The residue was taken up in benzene-d_6 and added to a new NMR tube to record the NMR spectra.

Proton resonances for the **4m** and **4r** compounds, according to the atomic number of the molecular structures [25] were as follows:

^1H NMR, **4m**: 3.5–3.7 (m), 3.9–4.05 (m), 6.6 (dd), 6.7 (dd), 7.0 (m), 7.15 (m), 7.5 (dt) ppm.

^1H NMR, **4r**: 3.6–3.9 (m), 6.2 (d), 6.5 (dd), 7.2 (m), 7.35 (m), 7.5 (dt) ppm

The same procedure was carried out with complexes **5m** and **5r**. According to the atomic numbering of the molecular structures [26], the NMR data for **5m** and **5r** were as follows:

- ^1H NMR, 5m: 2.38, 2.50, 3.5–3.8 (m), 3.8–4.15 (m), 6.70, 6.75, 6.80, 6.90 ppm.
- ^1H NMR, 5r: 2.3, 2.7, 3.5–3.8 (m), 4.0–4.35 (m), 6.30, 6.75, 6.80, 6.90 ppm.

The spectral data for complexes **4** and **5** are in good agreement with those previously reported [25,26] considering the differences in solvent. The photostationary state *racemic*/*meso* composition was determined by integrating the ^1H NMR spectra for the isomers. ^1H-NMR(C_6D_6): **4m** : **4r** and **5m** : **5r** 40:60.

For longer irradiation time ($t > 2$ h) the ^1H NMR analysis of the photolyzed solutions show the presence of free ligands [25,26] along with minor amounts of the $EBIZrCl_2$ and $EBDMIZrCl_2$ complexes.

2.3.3. Photochemical experiments in the ESR cavity

Spin trapping experiments were carried out in benzene and toluene solutions. Unless otherwise stated, solutions containing 0.1 M spin trap and 0.01 M complexes were used. A computer program developed by Dave Duling at NIEHS [27] was used for the simulation of the ESR spectra. Photolysis was carried out directly inside the cavity of the ESR spectrometer using a Hanau high pressure mercury lamp

Table 1
Spectral band maxima for zirconocene complexes in benzene

Complex	λ_{max} (nm)	ε ($M^{-1}\,cm^{-1}$)
1. Cp_2ZrCl_2	290	2394
	340	622
2. $Cp_2{}^*ZrCl_2$	350	1580
	370	1990
3. Ind_2ZrCl_2	310	1475
	380	720
4. $EBIZrCl_2$	352	
50:50 *meso* : *racemic*	383	
	428	
4r. $EBIZrCl_2$ *racemic*	429	1070
5m. EBDMI $ZrCl_2$ *meso*	380	1130
5r. $EBDMIZrCl_2$ *racemic*	425	1350

mounted on an optical bench and fitted with suitable filters in order to obtain the desired light frequencies.

Table 2
Hyperfine coupling constants of the observed radical-spin adducts

Complex	Spin trap			
	ND	PBN	DMPO	MNO_2P
1. Cp_2ZrCl_2	$a_N = 13.7$ G $a_H = 15.3$ G	$a_N = 14.6$ G $a_H = 2.9$ G	$a_N = 14.0$ G $a_H = 20.2$ G $a_H = 0.9$ G	$a_N = 26.8$ G
2. $Cp_2{}^*ZrCl_2$	$a_N = 13.5$ G	$a_N = 14.6$ G $a_H = 4$ G	$a_N = 14.8$ G $a_H = 20.3$ G	$a_N = 25.2$ G
3. Ind_2ZrCl_2	$a_N = 13.8$ G $a_H = 15.4$ G	$a_N = 14.6$ G $a_H = 2.5$ G		
4. $EBIZrCl_2$	$a_N = 13.8$ G $a_H = 14.5$ G $a_N = 13.7$ G	$a_N = 14.5$ G $a_H = 2.7$ G	$a_N = 14.0$ G $a_H = 21.2$ G $a_N = 14.1$ G $a_H = 22.6$ G	$a_N = 15.4$ G
5. $EBDMIZrCl_2$	$a_N = 14.0$ G $a_H = 9.8$ G $a_N = 13.7$ G	$a_N = 14.6$ G $a_H = 2.3$ G	$a_N = 14.3$ G $a_H = 20.4$ G $a_N = 14.3$ G $a_H = 21.9$ G	$a_N = 15.3$ G

3. Results and discussion

3.1. Electronic absorption spectra

The electronic absorption spectra data of a series of cyclopentadienyl and indenyl zirconium derivatives are reported in Table 1. Each spectrum shows a low energy band with $\varepsilon = 600/2000\,M^{-1}\,cm^{-1}$ followed by a more intense band with $\varepsilon = 1600/2500\,M^{-1}\,cm^{-1}$ in the high energy region. Since these are complexes of the d^0 Zr(IV), the observed bands must represent charge transfer transitions. The progressive red shift of the bands as the ligand changed from Cp to Cp* to Ind to *ansa* bis(indenyl) supports assigning the band as L–to–Zr (L = Cp, Cp*, Ind, EBI, EBDMI) charge transfer. Moreover, the first absorption maximum red sifts with the introduction of electron-releasing substituents in the ring and this is strictly analogous to what has been observed in metallocene electronic spectra [28].

One other compelling fact supporting the LMCT assignment is the calculated energy level ordering set [29] where the highest filled orbitals have mainly indenyl properties. The observed photochemistry of these complexes strongly suggests this interpretation as the reactive excited state associated to LMCT transition (vide infra).

3.2. Potochemistry

The experimental and theoretical observations reported above are consistent with the notion that the reactive excited state in the **1-5** complexes are of the L → Zr charge transfer type. Such 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 $L^\bullet$ and $[LZr^\bullet\, Cl_2]$ radicals.

To establish a benchmark for spectroscopic reference of this photoprocess, ESR experiments coupled with the spin trapping technique was first attempted. Thus, benzene solutions of complexes **1-3** were photolyzed in the presence of different spin traps specific for identification of organic- and metal-centered radicals [30,31]. Using nitroso and nitrone spin traps, fairly intense ESR signals of $L^\bullet$ spin adducts ($L^\bullet$=Cp **1**, Cp* **2**, Ind **3**) are observed. Hyperfine coupling constant values of these spin adducts are reported in Table 2.

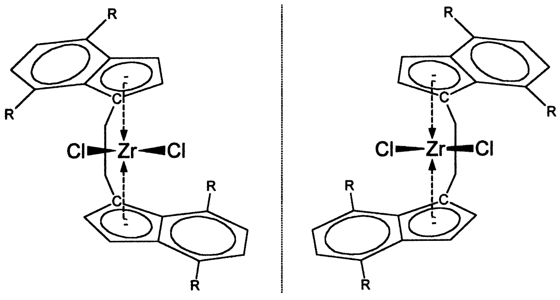
Using 2-methyl-2-nitropropane (MNO_2P) as a trapping agent for metal-centered radicals, the formation of a triplet 1 : 1 : 1 in intensity is observed. The hfcc values (Table 2) indicate the formation of t-BuN(O)OZr(L)Cl_2 adducts (L=Cp, Cp*, Ind). This assignment was supported by a computer simulation of the ESR spectrum using the parameters in Table 2 [27]. These results are remarkably consistent with those first reported for $(C_5H_5)_2ZrCl_2$ [32], with the photochemistry of zirconium complexes paralleling that of titanium derivatives. The chemistry indicated in Eq. (1) is quite clear on the basis of the ESR results and is consistent with a photoinduced cleavage of one of the L–Zr bonds as the primary excited state reaction.

$$\underset{\mathbf{1,2,3}}{L_2ZrCl_2} \xrightarrow[C_6H_6]{h\nu} L^\bullet + [LZr^\bullet Cl_2] \tag{1}$$

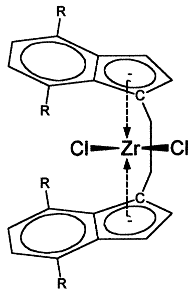
The photogenerated L $^\bullet$ and $[LZr^\bullet Cl_2]$ radicals are efficiently spin-trapped (Table 2). One result which leads to the conclusion that the primary photoprocess produces ligand and metal-centered radicals is the observed halide abstraction from CCl_4 by the $[LZr^\bullet Cl_2]$ intermediate when benzene solutions of **1-3** complexes were photolyzed in the presence of 1 M CCl_4 as reported in Eq. (2).

$$[LZr^\bullet Cl_2] + CCl_4 \xrightarrow{h\nu} LZrCl_3 + {}^\bullet CCl_3 \tag{2}$$

In the presence of nitrosodurene (ND) the ${}^\bullet CCl_3$ radicals are efficiently trapped (ND-CCl_3 adduct, $a_N = 10.63 \pm 0.05$ G, $a_H = 1.32 \pm 0.05$ G), the reaction in Eq. (2) occurs and conversion to $LZrCl_3$ takes place [33]. Apparently, chlorine abstraction from CCl_4 by Zr-centered radicals is a very



racemic mixture



meso isomer

Fig. 1. Illustration of the *meso* and *racemic* forms of $\mathrm{EBIZrCl_2}$ (R=H) and $\mathrm{EBDMIZrCl_2}$ ($\mathrm{R=CH_3}$).

efficient process since no Zr spin adducts could be detected when 1M $\mathrm{CCl_4}$ is present in the photolyzed benzene solution of **1-3** complexes.

Having labored to establish that the L–Zr bond cleavage is the only primary excited-state reaction in complexes **1-3**, we considered it timely to investigate the photoreactivity of the bridged complexes ethylene-bis(1-indenyl) zirconium dichloride ($\mathrm{EBIZrCl_2}$, **4**) and ethylene-bis(4,7-dimethyl-1-indenyl) zirconium dichloride ($\mathrm{EBDMIZrCl_2}$, **5**), whose structures are constrained by the $\mathrm{C_2}$ linkage joining the two indenyl systems [25,26]. The key point is that the complexes **4** and **5** exist in the *meso* (**4m**, **5m**) and *racemic* (**4r**, **5r**) forms (Fig. 1).

The electronic absorption data for the isomers are reported in Table 1. Consistent with the LMCT character of the transition, the absorption maximum red shifts with the introduction of electron-releasing substituents in the indenyl ring [28]. Quite interestingly, selective irradiation at 366 nm of the 50 : 50 **4m** : **4r** benzene solution causes a progressive increase of the band located at 429 nm, assigned to the *racemic* isomers **4r**, and a simultaneous decrease of the bands at 360 and 380 nm, both assigned to the *meso* **4m** isomer (Fig. 2).

Thus, these spectral variations can be interpreted in terms of the *meso*-to-*racemic* photoconversion **4m**→**4r**. In the early stage of photoreaction, the stoichiometry is almost clean and a fairly good isosbetic point is observed at about 390 nm. After 10 min of photolysis, a photostationary state is established between the isomers (Eq. (3)) with a *racemic* / *meso* (**4r** : **4m**) ratio of 60 : 40.

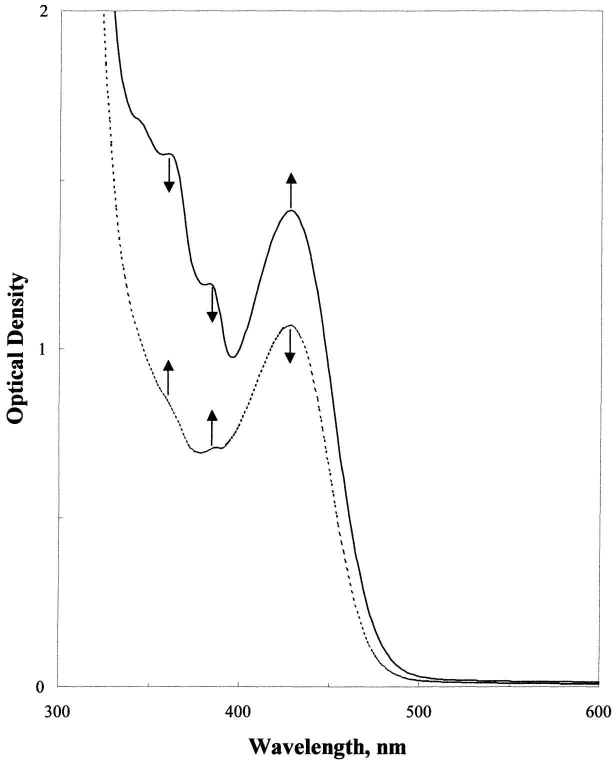


Fig. 2. Electronic absorption spectra of *racemic*-$\mathrm{EBIZrCl_2}$ (. . .) and of a 50:50 mixture of *meso*-$\mathrm{EBIZrCl_2}$ and *racemic*-$\mathrm{EBIZrCl_2}$ (—) at 298 K in benzene. The arrows indicate: (*i*) the decrease of the bands at 352, 383 nm and the increase of the band at 428 nm following photolysis at λ = 366 nm of the **4m** : **4r** mixture; (*ii*) the increase of the bands at 352, 383 nm and the decrease of the band at 428 nm accompanying the photolysis at λ = 436 nm of **4r**.

$$meso - \mathrm{EBIZrCl_2} \overset{h\nu}{\leftrightarrow} racemic - \mathrm{EBIZrCl_2} \qquad (3)$$

The electronic absorption spectral changes which occur upon photolysis of a benzene solution of $\mathrm{EBDMIZrCl_2}$ (50 : 50 **5m** : **5r** mixture) are reported in Fig. 3.

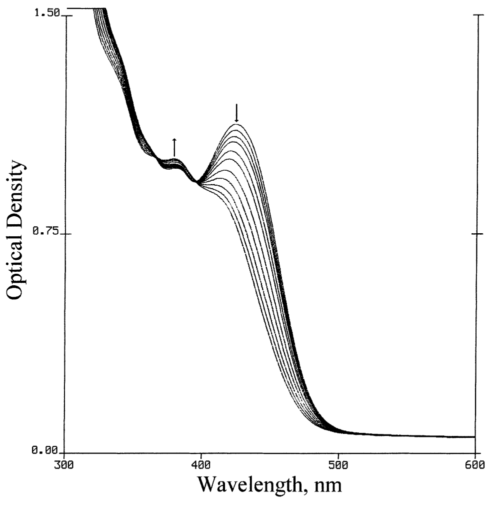


Fig. 3. Electronic spectral changes during λ = 436 nm photolysis of a 50 : 50 **5m** : **5r** benzene solution at 298 K.

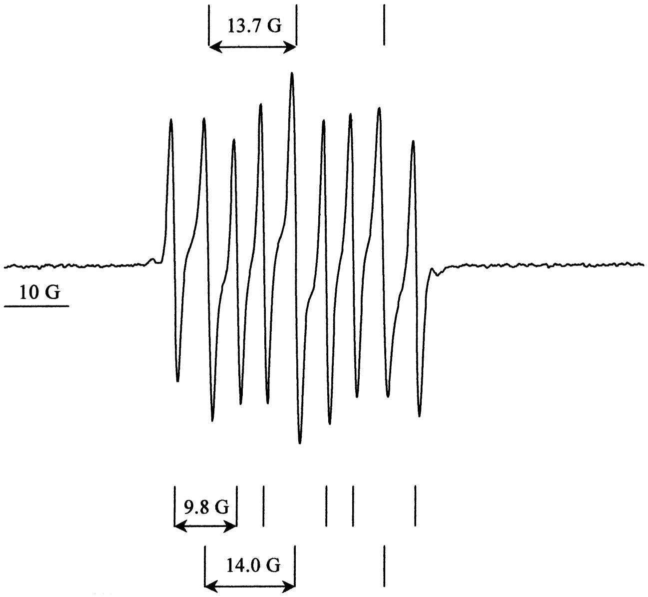


Fig. 4. EPR spectrum of the spin adducts formed during irradiation (λ = 366 nm) of a benzene solution of a *meso*-EBDMIZrCl_2 : *racemic*-EBDMIZrCl_2 (50 : 50) mixture in the presence of nitrosodurene. The hyperfine coupling constants are indicated in the stick diagram.

The isosbestic points observed and the electronic spectral changes suggest a conversion of *meso* **5m** to *racemic* **5r**. This photolysis also gave a photostationary mixture of the isomers with a **5r** : **5m** ratio of 60 : 40, calculated on the basis of the molar absortivities (vide infra).

To gain additional information on the nature of the photolysis of the **4** and **5** complexes,^{1}H NMR studies were carried out. After 25 min of NMR tube photolysis (λ = 366 nm) of a 50 : 50 mixture of the **4m** and **4r** isomers, the resonances for the **4r** complex had grown significantly in intensity and the resonances for the **4m** isomer had decreased proportionally. After 1 h of photolysis, the concentration of the *racemic* isomers remained static, resulting in a photostationary state with a *racemic* : *meso* ratio of 60 : 40. Similar results were obtained in the NMR tube photolysis of a 50 : 50 mixture of the isomers **5** (vide infra).

Other interesting experiments concerning the pure *racemic* complexes **4r** and **5r** have been performed. LMCT band irradiation at 436 nm of these complexes resulted in a bleaching of the respective absorption bands and concomitant formation of absorption bands of **4m** and **5m** complexes. A photostationary state is obtained with a *racemic* : *meso* ratio of 58 : 42. Thus, photolysis of *meso* and *racemic* mixtures of the **4** and **5** complexes gives stationary states rich in *racemic* complexes **4r** and **5r**. The production of *racemic* complexes **4r** and **5r** from the *meso* complexes **4m** and **5m** represents movement away the thermodynamic ratio of the two isomers. This reveal the direct intermediacy of an electronic excited state in the isomerization. Moreover, it is worth noting that the *racemic* : *meso* ratio obtained by direct photolysis of the *racemic* isomer is somewhat similar to that obtained by selective photolysis at 366 nm of the initial 50 : 50 mixture of **4m** an **4r** complexes. These experimental observations may be attributed to the formation of a common excited state for both reactions. The correlation could be rationalized merely assuming that photoexcitation causes the same dissociation of one of two L–Zr (L = EBI **4**, L = EBDMI **5**) bond with the possible formation of a biradical species which thermally rearranges to the static mixture of the two isomers. ESR experiments support this hypothesis. Thus, irradiation of a 50 : 50 5m : 5r benzene solution in the presence of nitrosodurene (ND) as spin trap, gives the ESR spectrum shown in Fig. 4.

The evident clue in the spectrum is the simultaneous formation of two features: one corresponding to a doublet of triplets; the other to a triplet as indicated by the stick diagram of Fig. 4. The two sets of coupling constant features could correspond to the formation of a biradical containing two unpaired electrons: one located on the indenyl ligand, the other on the Zr center in the same molecule. This postulate gains further experimental justification from the fact that the biradical does not react with CCl_4 to yield $\{ZrLCl_3\}$ as observed in the case of complexes **1-3**. The observation of the same ESR features from CT excitation of the **4m** : **4r** mixture can be similarly ascribed to a biradical. Taken together, these ESR results strongly suggests that the strap conformation of biradical allows faster conversion, principally to the more stable products (i.e., the *racemic* isomers) by rotation around the C–C bond of the ethylene bridge (Fig. 5). Such behavior is to be expected since greater inter-ring interactions can be anticipated for meso isomers [25,26].

Accompanying the isomeric interconversion at longer photolysis times, some decomposition was seen as indicated

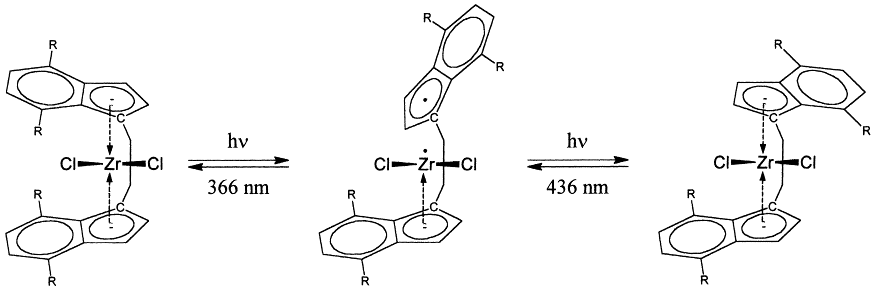


Fig. 5. Schematic representation of the *meso*-to-*racemic* photoconversion through the formation of a biradical intermediate.

by the presence of free EBI or EBDMI ligands (detected by ^{1}H NMR in tube photolysis). This might be due to a side reaction of biradicals, consistent with hydrogen abstraction from the solvent. Much research remains to be conducted on *ansa* metallocenes. Characterization of the full nature of the excited states will prove particularly important in improving the *meso*-to-*racemic* photoisomerization of *ansa*-zirconocenes.

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