# Photochemistry and Emission Behaviour of the Iron(II) Mixed Metallocene Complexes [$C_5R_5Fe(arene)$]$PF_6$ (R = H or Me)

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Mixed metallocenes of general formula [$(\eta^5\text{-}C_5R_5)Fe^+(\eta^6\text{-arene})$] (R = H or Me), irradiated at long wavelengths (> 320 nm) show a fluorescence band centred at 520 nm. Fluorescence yields are strongly dependent upon the arene, and range from $1.2 \times 10^{-3}$ for [$CpFe^+$(*p*-dimethoxybenzene)] (Cp = $C_5H_5$), to less than $0.2 \times 10^{-4}$ when the arene is benzene, toluene, mesitylene, or pentamethylbenzene. The fluorescence quantum yields obtained upon irradiation of [$CpFe^+$(*p*-xylene)] increase when hexamethylbenzene (HMB) is added, and approach, at high HMB concentrations, a value of $8 \times 10^{-4}$, similar to that obtained when [$CpFe^+$(HMB)] is irradiated. These results are explained in terms of an efficient ligand exchange on the excited surface. Hexamethyl(dewar benzene) (HMDB) increases the fluorescence of [$CpFe^+$(*p*-xylene)] and decreases the fluorescence emitted by [$CpFe^+$(*p*-dimethoxybenzene)]. In both systems the fluorescence yields can be extrapolated, at high [HMDB], to the value observed when [$CpFe^+$(HMB)] is irradiated. These results are compatible with both the occurrence of an efficient valence isomerization of HMDB and ligand exchange on the excited surface.

There are several reviews on the photochemistry and photophysics of sandwich organometallic compounds [$(C_5H_5)_2M$] (M = transition metal).[1-5] The currently available information provides a clear picture regarding the energetics and spectroscopic characterization of the excited states.[5] One of the most studied photochemical processes is photo-oxidation, which takes place by a charge-transfer mechanism involving the interaction of electron-accepting solvents with the excited complex.[4] Other photoprocesses appear to be promoted by homolytic cleavage of the cyclopentadienyl ring, leading to ligand exchange.[4] With regard to luminescence, it has been reported only that ruthenocene,[4] $(C_5H_5)_2Ru$, shows a ligand field emission from a $^3E_1$ ligand field triplet. Ferrocene, $(C_5H_5)_2Fe$, has been the subject of several studies and it now appears that earlier reports[6] of its luminescence are in error. The closely related cationic mixed metallocenes of $d^6$ iron, [$(C_5R_5)Fe(C_6H_{6-n}Me_n)$]$^+$ (R = H or Me; *n* = 0—6), have been extensively studied with regard to their electrochemical[7a] and spectroscopic[7b-d] properties and their chemical reactivity, being the subject of several recent reviews.[8-10] The photochemistry of these compounds is strongly dependent both on the irradiation wavelength and the solvent. When the irradiation is carried out at long wavelengths (440 nm, corresponding to the $^1A_1 \longrightarrow {}^1E_1$ transition[5,11]) in solvents of low donor number (0—14),[12] a regioselective photoexchange takes place. The process occurs *via* a photogenerated coordinatively unsaturated intermediate stabilized by basic two- and six-electron ligands.[13] The $^1E_1$ excited singlet can lead, through intersystem crossing, to the $^3E_1$ state with a weakening of the metal–arene bond that favours dissociation of the complex.[13-15] The only reported emission from a mixed metallocene was observed by our group in the photocatalysed valence isomerization of hexamethyl(dewar benzene) (HMDB),[16] and was assigned to an exciplex adduct. In order to clarify further the source of the emission, we have carried out a study of the photophysics of several mixed metallocenes. Furthermore, the effects of added arenes and HMDB upon their photobehaviour have been evaluated. The mixed metallocenes considered were of the general formula [$(\eta^5\text{-}C_5R_5)Fe^+(\eta^6\text{-arene})$] with R = H or Me and arene = benzene, toluene, *p*-xylene, mesitylene, 1,2,4,5-tetramethylbenzene (durene), pentamethylbenzene, HMB, *p*-dimethoxybenzene, or hexaethylbenzene.

## Experimental

*Materials.*—All mixed cationic metallocenes of the [$C_5H_5Fe^+$(arene)] series were prepared by the method of Nesmeyanov.[17] [$C_5Me_5Fe^+$(*p*-xylene)] was prepared according to Coffield's method,[18] and [$CpFe^+$(hexaethylbenzene)] by permethylation of [$CpFe^+$(HMB)].[19] All compounds were isolated as hexafluorophosphate salts, and purified by recrystallization from acetone and by alumina column chromatography. Their purity was verified by microanalysis (C, H, P, and Fe) and $^1H$ n.m.r. (100 MHz). Hexamethyl(dewar benzene) (HMDB) (Aldrich) was distilled under reduced pressure and stored in the dark under argon at −4 °C. All solvents used were of spectroscopic grade.

*Luminescence Spectra.*—Luminescence spectra were recorded in dichloromethane with a Perkin-Elmer 650-10S spectrofluorimeter, under either argon or oxygen atmosphere at room temperature (22 °C). Excitation was carried out by a Nitronite nitrogen laser (λ 337 nm); signals were recorded by a Tektronic oscilloscope. For quantum yield and fluorescence-quenching experiments, solutions were purged and saturated with argon by the syringe bubbling technique. The excitation spectra of 0.05, 0.01, and 0.0008M-solutions of [CpFe(*p*-xylene)]$PF_6$ were recorded in dichloromethane as solvent.

*Emission Quantum Yield Measurement Procedure for* [$C_5R_5Fe$(*arene*)]$PF_6$ (R = H *or* Me).—Emission quantum yields for [$C_5R_5Fe$(arene)]$PF_6$ were determined with dichloromethane as solvent by using the fluorescence[20] of benzil ($\Phi_{fl.} = 10^{-3}$) as primary standard ($\lambda_{exc.}$ 430 nm). Comparisons of the areas under the emission spectra were carried out under matched absorbance conditions, for the benzil and the corresponding cationic complexes. The areas under the spectra were calculated by triangulation and corrected by Simpson's method.

**Table.** Emission yields[a]

| Compound[b] | $10^4\Phi_E$ |
|---|---|
| [CpFe$^+$(benzene)] | <0.2 |
| [CpFe$^+$(toluene)] | <0.2 |
| [CpFe$^+$(*p*-xylene)] | 0.9 |
| [CpFe$^+$(mesitylene)] | <0.2 |
| [CpFe$^+$(durene)] | 4.4 |
| [CpFe$^+$(pentamethylbenzene)] | <0.2 |
| [CpFe$^+$(hexamethylbenzene)] | 7.3 |
| [CpFe$^+$(hexaethylbenzene)] | 4.6 |
| [CpFe$^+$(*p*-dimethoxybenzene)] | 12.0 |
| [$C_5Me_5Fe^+$(*p*-xylene)] | 1.3 |

[a] Dichloromethane solution of [CpFe(arene)]$PF_6$; fluorescence of benzil as standard ($\Phi_{fl.} = 10^{-3}$). [b] All the cationic compounds [CpFe$^+$(arene)], have $PF_6^-$ as counterion.

*Fluorescence-quenching Experiments.*—Quenching experiments for [CpFe(arene)]$PF_6$ fluorescence in dichloromethane were carried out by using dimethylaniline (DMA) as quencher, added in various concentrations to 0.02M-[CpFe(arene)]$PF_6$ in dichloromethane. No shape change was observed in the fluorescence spectra, but their intensity changed upon addition of DMA. A Stern–Volmer relationship was observed between the ratio of the fluorescence intensities in the absence and presence of the quencher ($I_0/I$) and [DMA]: $I_0/I = 1 + k_Q\tau$[DMA] where $k_Q$ is the quenching rate constant and $\tau$ is the fluorescence lifetime of [CpFe$^+$(arene)].

*Effects of Addition of HMDB or HMB on the Fluorescence of* [CpFe(arene)]$PF_6$.—Increasing amounts of HMDB or HMB were added to a 0.01M-solution of [CpFe$^+$(*p*-xylene)]$PF_6$ in dichloromethane and the corresponding emission spectra ($\lambda_{em.}^{max.}$ 520 nm) were recorded. There was no change in shape but a change in intensity on addition of HMDB or HMB. The change in fluorescence intensity occurred for short periods of time, independent of the irradiation time. Values of $\Phi$ were measured at very short irradiation times to avoid excitation of the complexes that could be produced by ligand photo-exchange. Linear plots of $1/\Phi_E$ *versus* 1/[HMB], or $1/\Phi_E$ *versus* 1/[HMDB], were obtained.

## Results and Discussion

*Luminescence from Mixed Metallocene Complexes.*—Emission spectra (uncorrected) of [CpFe$^+$(HMB)] and [CpFe$^+$(*p*-xylene)] obtained after excitation with light of wavelength 430 nm under similar conditions in dichloromethane are shown in Figure 1, which also includes the emission detected when the solvent was irradiated under identical conditions. The figure shows conclusively that both compounds present a significant luminescence centred at 520 nm, and that emission yields are strongly dependent upon the arene. Furthermore, the observed luminescence was not sensitive to further purification of the cationic complexes, showing that it cannot be due to adventitious impurities.

Excitation spectra ($\lambda_{em.}$ = 520 nm) were recorded for [CpFe$^+$(*p*-xylene)] and [CpFe$^+$(HMB)]. Both spectra show two broad bands of similar intensities centered near 370 and 470 nm. Absorption spectra of these mixed metallocenes show, at long wavelengths, a very broad band with two maxima near 460 and 380 nm.[13] At wavelengths shorter than 320 nm, a more intense band is observed in the absorption spectrum, but this band is absent from the excitation spectrum. A comparison of both spectra indicates that emission is associated with excitation to the low-energy ligand field states of the mixed metallocene complexes.

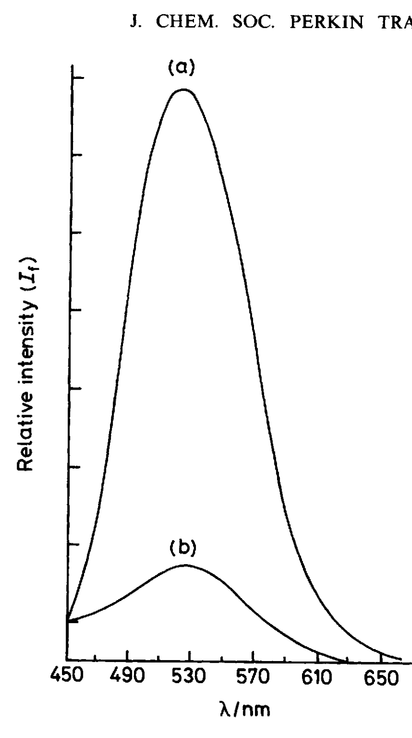

**Figure 1.** Fluorescence spectra of (a) [CpFe$^+$(HMB)]$PF_6$ and (b) [(CpFe$^+$(*p*-xylene)]$PF_6$ (both 2 × $10^{-2}$M in dichloromethane); excitation wavelength 430 nm; room temperature

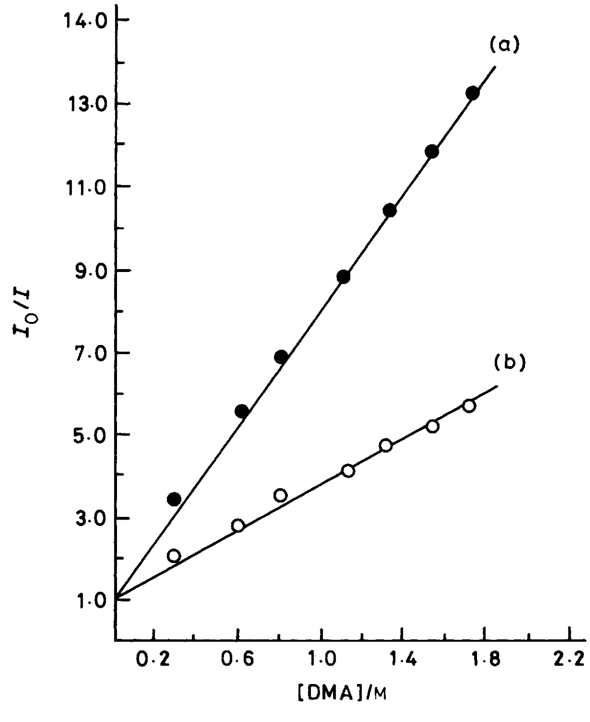

**Figure 2.** Stern–Volmer plots for the quenching of the emission of (a) [CpFe$^+$(HMB)]$PF_6$, $k_Q\tau$ = 7 dm$^3$ mol$^{-1}$, and (b) [CpFe$^+$(*p*-xylene)]$PF_6$, $k_Q\tau$ = 2.4 dm$^3$ mol$^{-1}$; both complexes in dichloromethane with dimethylaniline (DMA) as quencher; excitation wavelength 370 nm; room temperature

Emission yields were obtained by employing benzil as a standard. This compound has a fluorescence band ($\Phi_{fl.} = 10^{-3}$) which closely resembles, in position and shape,[20] that of the compounds considered in the present work. Since emission

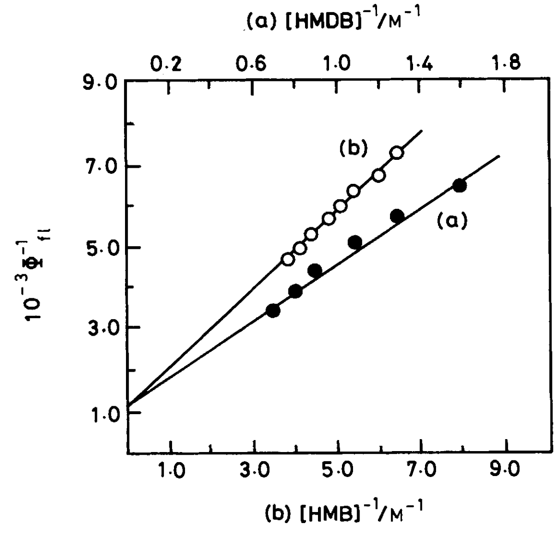

**Figure 3.** Dependence of fluorescence quantum yield on addition of (a) hexamethyl(dewar benzene), (HMDB) or (b) hexamethylbenzene (HMB) to a dichloromethane solution of [CpFe$^+$($p$-xylene)]PF$_6$ ($10^{-2}$M), $\Phi_{fl,\infty} = 8 \times 10^{-4}$, determined from the same intercept

spectra are uncorrected, matching of the bands of the standards to the considered compound is required to minimize the error of the method. Furthermore, since all compounds have similar emission bands, relative emission yields can be obtained with high accuracy, independent of the standard employed. Emission yields obtained by this procedure are given in the Table.

The luminescence can be quenched by dimethylaniline. The results obtained, plotted according to the Stern–Volmer equation, are shown in Figure 2. The fact that the plots are linear up to $I_0/I$ values as high as 13 indicates that the luminescence observed is being emitted from a single excited state. Furthermore, the $k_Q\tau$ values obtained are 7.0 and 2.4 dm$^3$ mol$^{-1}$ for [CpFe$^+$(HMB)] and [CpFe$^+$($p$-xylene)], respectively. The larger value for the former compound is compatible with its larger $\Phi_E$ value and suggests its longer lifetime. Attempts to measure directly the singlet lifetime by following the luminescence decay after excitation with a pulse from a nitrogen laser (λ 337 nm) were unsuccessful, since the decay was faster than the detection limit of the system employed (*ca.* 7 s). These short lifetimes are also supported by the fact that the observed luminescence is nearly independent of the presence of oxygen (up to 1 atm).

In conclusion, all the data indicate that the observed luminescence corresponds to fluorescence emitted by an excited [CpFe$^+$(arene)]* complex of very short lifetime. This is supported by the small energy gap observed between the excitation and emission bands and the fact that the emitted luminescence has an energy larger than that of the $S_0 \longrightarrow T_1$ transition.[13c]

Fluorescence yields in the Table show that only compounds with two perpendicular $C_2'$ symmetric axes in the plane of the arene have measurable fluorescence yields. For these compounds, the fluorescence yields increase with the number of methyl substituents, and are larger for methoxy- than for methyl-substituted arenes. All these results indicate that emission yields increase as the electron density of the arene ring increases. Also, methyl substitution in the cyclopentadienyl ring moderately increases the observed luminescence.

*Effect of Added Hexamethylbenzene*.—The emission yield of a given [CpFe$^+$(arene)] is sensitive to the presence of other arenes. A detailed study was carried out on the effect of added HMB upon the emission yield obtained in the irradiation of [CpFe$^+$($p$-xylene)]. The results, plotted as $\Phi_E^{-1}$ against [HMB]$^{-1}$, are given in Figure 3. This Figure shows a nearly linear dependence, with an intercept of $1.12 \times 10^3$. The emission yield at 'infinite' [HMB] is then $8 \times 10^{-4}$, close to that obtained when the [CpFe$^+$(HMB)] complex is directly irradiated. Furthermore, the increase in emission takes place without noticeable changes in the spectral distribution. These facts, together with the linear dependence shown in Figure 3, are compatible with the reaction scheme shown (Scheme 1),

$$[\mathrm{CpFe}^+(p\text{-xylene})] + h\nu \longrightarrow [\mathrm{CpFe}^+(p\text{-xylene})]^* \qquad (1)$$

$$[\mathrm{CpFe}^+(p\text{-xylene})]^* \longrightarrow (h\nu)_{fl} + [\mathrm{CpFe}^+(p\text{-xylene})] \qquad (2)$$

$$[\mathrm{CpFe}^+(p\text{-xylene})]^* \longrightarrow [\mathrm{CpFe}^+(p\text{-xylene})] \qquad (2')$$

$$[\mathrm{CpFe}^+(p\text{-xylene})]^* + \mathrm{HMB} \longrightarrow [\mathrm{CpFe}^+(\mathrm{HMB})]^* + p\text{-xylene} \qquad (3)$$

$$[\mathrm{CpFe}^+(\mathrm{HMB})]^* \longrightarrow (h\nu)_{fl} + [\mathrm{CpFe}^+(\mathrm{HMB})] \qquad (4)$$

$$[\mathrm{CpFe}^+(\mathrm{HMB})]^* \longrightarrow [\mathrm{CpFe}^+(\mathrm{HMB})] \qquad (4')$$

**Scheme 1.**

which includes ligand exchange from the excited [CpFe$^+$(arene)]* complex. This simple scheme predicts that the observed emission yield Φ is given by equation (5), where $\Phi^0_{I}[\equiv k_2/(k_2 + k'_2)]$ and $\Phi^0_{II}[\equiv k_4/(k_4 + k'_4)]$ are the fluorescence yields of [CpFe$^+$($p$-xylene)] and [CpFe$^+$(HMB)], respectively. Under conditions such that $\Phi \gg \Phi^0_I$ and/or $k_3[\mathrm{HMB}] \gg k_2 + k'_2$, equation (5) can be reduced to equation (6), where $\tau_I$ is the [CpFe$^+$($p$-xylene)] lifetime. Equation (6) agrees with the observed behaviour.

$$\Phi = \frac{k_3[\mathrm{HMB}]}{k_2 + k'_2 + k_3[\mathrm{HMB}]}\Phi^0_{II} + \frac{k_2 + k'_2}{k_2 + k'_2 + k_3[\mathrm{HMB}]}\Phi^0_{I} \qquad (5)$$

$$\Phi^{-1} = \Phi^0{}_{II}^{-1} + \Phi^0{}_{II}^{-1}(k_3\tau_I)^{-1}\,[\mathrm{HMB}]^{-1} \qquad (6)$$

The effect of added HMB can then be explained in terms of ligand exchange on the excited singlet surface, followed by normal emission from the excited state produced. This conclusion is different from, but not contradictory to, the proposal that the lowest triplet state is involved in the photochemical removal of the arene induced by nucleophilic interactions with the medium.[13c,15] The fact that at very high HMB concentrations the observed yields approach that obtained in the direct irradiation of [CpFe$^+$(HMB)] indicates that ligand exchange is an efficient process that takes place without significant deactivation of the excited mixed metallocene complex. From the slope and intercept of Figure 3, $k_3\tau_I$ = 1.3 dm$^3$ mol$^{-1}$ is obtained. Since $\tau_I < 7$ ns, $k_2$ must be greater than $2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, indicating that ligand exchange on the excited surface is a very fast process.

*Effect of Hexamethyl(dewar benzene) Addition*.—HMDB addition to [CpFe$^+$($p$-xylene)] produces changes similar to those observed when HMB is added. The luminescence increases without significant changes in spectral distribution. The change in luminescence intensity as a function of HMDB concentration is shown in Figure 2. A linear dependence according to equation (6) is obtained, with a limiting value for the fluorescence yield of $8 \times 10^{-4}$ and a slope of $3.3 \times 10^3$ dm$^3$

$\mathrm{mol}^{-1}$. These results can be interpreted in terms of a reaction scheme similar to that proposed for HMB. The critical excited state process can now be represented by reaction (7), which

$$\mathrm{HMDB} + [\mathrm{CpFe}^+(p\text{-xylene})]^* \longrightarrow p\text{-xylene} + [\mathrm{CpFe}^+(\mathrm{HMB})]^* \tag{7}$$

involves valence isomerization and exchange on the excited surface. The fact that the extrapolated value for the emission yield is equal to that obtained when $[\mathrm{CpFe}^+(\mathrm{HMB})]$ is irradiated directly implies that reaction (7) takes place without significant deactivation. Furthermore, from the slope and intercept $k_7\tau_1 = 0.4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}$ is obtained. Reaction (7), although highly efficient, is then considerably slower than reaction (3), which involves exchange without valence isomerization.

The results obtained when HMDB is added to $[\mathrm{CpFe}^+(\mathrm{HMB})]$, $[\mathrm{CpFe}^+(p\text{-dimethoxybenzene})]$, and $[\mathrm{C_5Me_5Fe}^+(p\text{-xylene})]$ are also in agreement with the occurrence of reaction (7). Addition of HMDB to $[\mathrm{CpFe}^+(p\text{-dimethoxybenzene})]$ produces a progressive decrease of the fluorescence down to a yield near $7.5 \times 10^{-4}$, a result compatible with the occurrence of reaction (8) with high efficiency. On the other hand, HMDB has

$$[\mathrm{CpFe}^+(p\text{-dimethoxybenzene})]^* + \mathrm{HMDB} \longrightarrow [\mathrm{CpFe}^+(\mathrm{HMB})]^* + p\text{-dimethoxybenzene} \tag{8}$$

no significant effect when added to $[\mathrm{CpFe}^+(\mathrm{HMB})]$ or $[\mathrm{C_5Me_5Fe}^+(p\text{-xylene})]$. The former result is expected if isomerization takes place without significant deactivation. The lack of effect observed in the irradiation of the permethylated compounds is compatible with the reported lack of reactivity of these compounds in ligand photoexchange processes.[13f,15]

The detailed mechanism of the isomerization and exchange process cannot be conclusively deduced from the present data. Nevertheless, it could be represented by the Scheme 2, where

$$[\mathrm{CpFe}^+(\mathrm{arene})]^* + \mathrm{HMDB} \rightleftharpoons \underset{\mathrm{Ex_I}}{[\mathrm{CpFe}^+(\mathrm{arene})\ldots(\mathrm{HMDB})]^*} \tag{9}$$

$$\mathrm{Ex_I} \longrightarrow \underset{\mathrm{Ex_{II}}}{[\mathrm{CpFe}^+(\mathrm{arene})\ldots(\mathrm{HMB})]^*} \tag{10}$$

$$\mathrm{Ex_{II}} \longrightarrow \underset{\mathrm{Ex_{III}}}{[\mathrm{CpFe}^+(\mathrm{HMB})\ldots(\mathrm{arene})]^*} \tag{11}$$

$$\mathrm{Ex_{III}} \longrightarrow [\mathrm{CpFe}^+(\mathrm{HMB})]^* + \mathrm{arene} \tag{12}$$

**Scheme 2.**

process (9) represents the reversible formation of a $[\mathrm{CpFe}^+(\mathrm{arene})\ldots(\mathrm{HMDB})]^+$ exciplex, and process (12) the dissociation of a $[\mathrm{CpFe}^+(\mathrm{HMB})\ldots(\mathrm{arene})]^*$ exciplex. The formation of HMDB and HMB exciplexes from both excited singlet and triplet states has been reported.[21] Valence isomerization of HMDB exciplexes in nonpolar solvents to produce HMB exciplexes has also been reported.[22] In particular, Jones and Becker have observed very large yields of adiabatic isomerizations of excited singlet complexes formed between excited electron acceptors and HMDB.[23]

The occurrence of reaction (10) provides a photochemical path for the valence isomerization of HMDB. Nevertheless, this process cannot be the main reaction path involved when the isomerization is catalysed by mixed metallocene complexes, since quantum yields considerably larger than one are generally observed,[13f] this being indicative of a chain process.

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