Photo-activated Valence Isomerization of Hexamethyl(Dewar benzene) (HMDB) assisted by Arene–Iron(II) Complexes: Luminescence Properties of $[\mathrm{HMDB}\cdots(\eta^5\text{-}C_5R_5)\overset{+}{Fe}(\eta^6\text{-arene})]^*$ Adducts

Enrique Román,* Sergio Hernández, and Mauricio Barrera

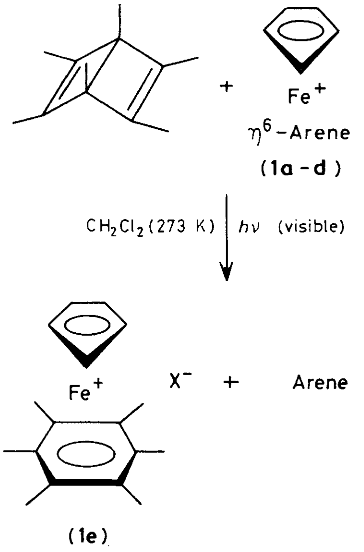
Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 114-D, Santiago, Chile

Hexamethyl(Dewar benzene) (HMDB) isomerizes to hexamethylbenzene (HMB) under visible light irradiation in the presence of stoicheiometric or catalytic amounts of the cationic complexes $[(\eta^5\text{-}C_5R_5)Fe(\eta^6\text{-arene})]^+X^-$, (R = H, Me; X = BF_4^-, PF_6^-), (**1a—e**) and (**2**), in dichloromethane solutions at 273 K; mixtures of HMDB and (**1b—e**) or (**2**) in dichloromethane exhibit a luminescence band at 530—540 nm probably due to formation of the corresponding exciplex.

The isomerization of hexamethyl(Dewar benzene) (HMDB) to hexamethylbenzene (HMB), catalysed by rhodium(I) and palladium(II) complexes under thermal conditions has already been studied.[1] We now report the first example of the photo-catalysed isomerization of HMDB to HMB by the light-induced action of the $[(\eta^5\text{-}C_5R_5)Fe(\eta^6\text{-arene})]^+X^-$ complexes (**1a—e**) and (**2**).

Irradiation with visible light (sun lamp, 200 W; pyrex cell) of a solution of 0.2 mmol of (**1a**) and 0.2 mmol of HMDB in 2 ml of dichloromethane for 1 h at 273 K gave complex (**1e**) and naphthalene quantitatively; (**1e**) was precipitated (yield 95%) by addition of diethyl ether (Scheme 1). Under similar conditions, the analogous complexes (**1b**), (**1c**), and (**1d**) afforded (**1e**) and the corresponding arene. The irradiation of dichloromethane solutions of HMDB in the presence of stoicheiometric amounts of (**1e**) or the *p*-xylene derivative (**2**) (273 K) led to complete isomerization of the HMDB to give HMB. Complex (**1e**) or (**2**), respectively, was recovered quantitatively by addition of diethyl ether (Scheme 2). The arene ligands in (**1e**) and (**2**) were not displaced.[2] However, the complete HMDB → HMB isomerization in the presence of (**1e**) or (**2**) required a prolonged irradiation [15 h as compared to 1 h for (**1a—d**)].

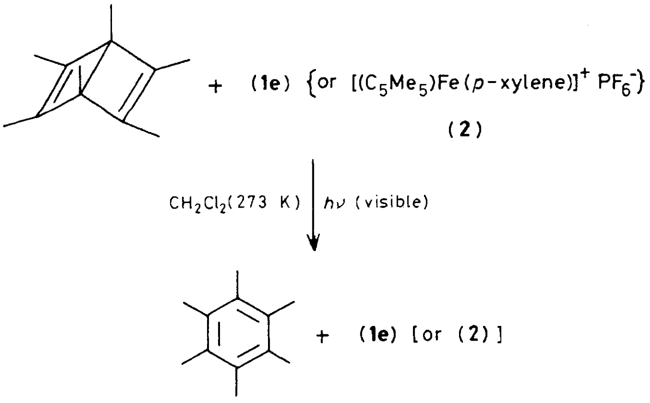
The photo-activated HMDB → HMB isomerization was also carried out using only catalytic amounts (5%) of the complexes (**1a—e**) or (**2**). The conversions were monitored by ^1H n.m.r. spectroscopy in CD_2Cl_2 [δ 1.67 and 1.14 (HMDB); 2.26 (HMB)]. In the dark, none of the complexes (**1a—e**) or (**2**) caused HMDB to isomerize within 3 h, but under visible light the signal due to free HMB appeared and increased progressively. The isomerization rate depends upon the nature of the co-ordinated ligand in the catalyst: a fast reaction was observed for (**1a**) (half life for HMDB, τ = 23 min) and a relatively slow reaction occurred with (**2**), (τ = 300 min). The sequence found for the isomerization rate [(**1a**) $\gg$ (**1b**) > (**1c**) > (**1d**) $\gg$ (**1e**) > (**2**)] corresponds to the lability of the η^6-arene–iron bond in the organometallic complexes (**1a—e**) and (**2**) under visible light.[2] Under the same conditions of irradiation, but without the organometallic complexes (**1a—e**) or (**2**) (273 K, solvent CD_2Cl_2, degassed solution, λ > 400 nm) and with monitoring by ^1H n.m.r. spectroscopy, the HMDB



—: Me

	Arene	X⁻
(**1**) a;	Naphthalene	PF_6^-
b;	Benzene	BF_4^-
c;	*p*-Xylene	PF_6^-
d;	Durene	BF_4^-

Scheme 1



Scheme 2

Table 1. Emission and absorption spectra.[a]

System	Emission, λ_{max}/nm	Absorption, λ_{max}/nm[b]	
HMDB	—	—	
HMB	—	—	
Naphthalene	416	—	
(**1a**) + HMDB	—	481(173)	360(402)
(**1b**) + HMDB	534	451(61)	381(80)
(**1c**) + HMDB	540	452(64)	389(86)
(**1d**) + HMDB	535	455(66)	403(85)
(**1e**) + HMDB	530	450(87)	388(87)
(**2**) + HMDB	532	453(75)	380(85)

[a] All the emission and absorption spectra were recorded in dichloromethane at 273 K. [b] Values in parentheses indicate the molar extinction coefficient ε/dm^3 mol^{-1} cm^{-1}.

→ HMB photo-isomerization was shown to be very slow (*ca.* 5% conversion after 5 h). This is probably explained by the presence of traces of HCl in the solvent that would activate an ion-induced radical photoreaction.[4]

The calculated activation energy of the electrocyclic HMDB → HMB opening is 154.8 kJ mol^{-1}.[3] Hence, the $[(\eta^5\text{-}C_5R_5)Fe(\eta^6\text{-arene})]^+$ system is a convenient catalyst for this process under mild conditions. In an attempt to understand the nature of the isomerization process, the absorption and emission properties of solutions of the complexes (**1a**—**e**) and (**2**) and those of their mixtures with HMDB were studied (*e.g.* Figure 1). For both HMDB and HMB, and the complexes (**1a**—**e**) and (**2**) no emissions were observed, but for the mixtures of (**1b**—**e**) or (**2**) with HMDB, a characteristic luminescence was observed (in dichloromethane, 0.25—0.5 M of mixture; 273 K).† The position of the emission band at 530—540 nm is little affected by change in the arene ligand (Table 1); the luminescence intensity increased linearly with the concentration of the complexes. This luminescence phenomenon is indicative of the formation of an exciplex species $[\text{HMDB}\cdots\cdot(\eta^5\text{-}C_5R_5)\overset{+}{\text{Fe}}(\eta^6\text{-arene})]^*$. The luminescence decay at 273 K, observed under visible light irradiation and measured as log (I/I_0), decreased linearly with time, consistent with a first order rate process (Figure 1).

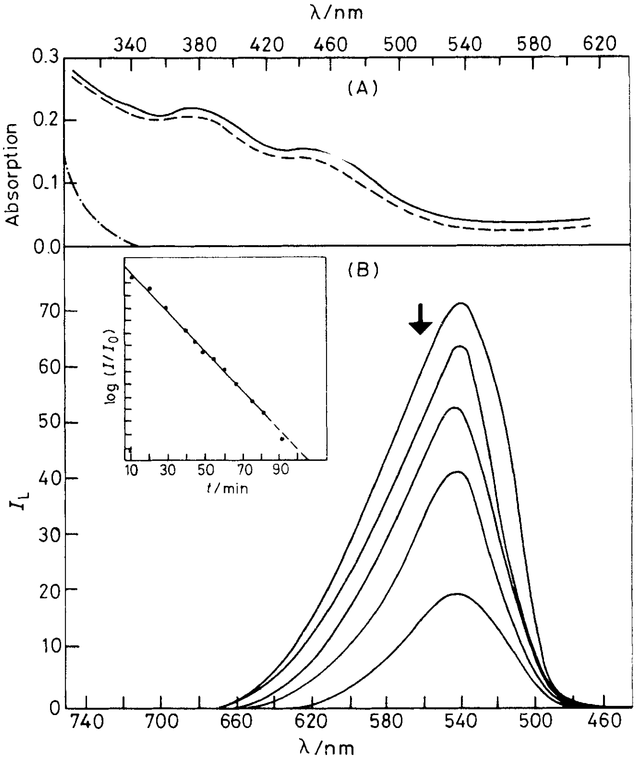


Figure 1. (A) Absorption spectra of solutions of (**1c**) (———), HMDB (-·-·-), and (**1c**) + HMDB (- - -) (all 0.05 M in dichloromethane; 273 K). (B) Emission spectra of (**1c**) + HMDB. The luminescence decays linearly with increasing time both of the irradiation and of the HMDB → HMB isomerization.

These results suggest two possible mechanisms for the HMDB → HMB isomerization: (i) dissociation of the exciplex $[\text{HMDB}\cdots(\eta^5\text{-}C_5R_5)\overset{+}{\text{Fe}}(\eta^6\text{-arene})]$ giving rise to an ionic chain reaction HMDB → HMDB$^{\cdot+}$ → HMB$^{\cdot+}$ → HMB + HMDB$^{\cdot+}$ . . . as postulated for this conversion in the presence of organic electron acceptors in polar media.[4] (ii) Photoinduced internal electron transfer within the exciplex state, leading to an isomerized exciplex adduct, as observed in similar systems containing electron acceptors such as diethyl dicyanofumarate, tetracyanobenzene, and tetracyanoquinodimethane.[5]

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† The same emission phenomenon, without a significant change in shape and position of spectra, was observed for mixtures of (**1b**—**d**) or (**2**) and HMDB in other solvents, *e.g.* acetone, acetonitrile, and nitromethane. The observed luminescence intensities follow the order: acetone > MeCN > CH_2Cl_2 > $MeNO_2$, for the same HMDB-complex concentrations (0.05 M).

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