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MASS SPECTROMETRY OF TRANSITION METAL π-COMPLEXES

VI*. π-CYCLOPENTADIENYL(CYCLOHEXADIENYL)IRON DERIVATIVES

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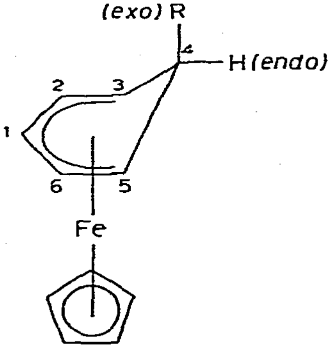
Summary

Mass spectra of *exo*-R-cyclohexadienyl(cyclopentadienyl)iron derivatives have been studied to show that the main fragmentation routes involve stereoselective migration of the *endo*-hydrogen of the cyclohexadienyl ring to the iron.

Fragmentation of π-cyclohexadiene and π-cyclohexadienyl transition metals complexes under electron impact is characteristic in that dehydrogenation occurs (a hydrogen molecule is eliminated from the cyclohexadiene ring or a hydrogen atom from the cyclohexadienyl) and results in σ—π ions of the type $[C_6H_6M]^+$ (M is a transition metal) [1-6]. *Exo*-D-analogues of cyclohexadiene-iron tricarbonyl [1] and cyclohexadienyl(cyclopentadienyl)iron [2] were ana-



I R = H ; II R = D ; III R = CH_3 ; IV R = C_2H_5 ; V R = C_6H_5 ; VI R = CCl_3

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* For part V see ref. 9.

TABLE 1

RELATIVE INTENSITIES IN THE MASS SPECTRA OF *exo*-SUBSTITUTED CYCLOHEXADIENYL-(CYCLOPENTADIENYL)IRON IONS ($\%/\Sigma_{50}$)

Ion	Ionising voltage (eV)	R					
		C_6H_5	H	D	CH_3	C_2H_5	CCl_3
$RC_6H_6FeC_5H_5^+ [P^+]$	15	39.5	37.1	27.7	22.2	5.3	0
	50	10.4	7.2	5.3	6.1	1.2	0
$RC_6H_5FeC_5H_5^+ [P-H]^+$	15	20.9	29.3	22.7	7.3	2.2	0
	50	13.1	8.2	5.9	4.9	9.9	0
$C_6H_6FeC_5H_5^+ [P-R]^+$	15	5.9		2.7	25.3	41.1	25.1
	50	4.5		0.8	10.1	13.4	10.4
$RC_6H_5Fe^+ [P-C_5H_6]^+$	15	0.8	7.9	7.1[a]	4.3	2.6	0
	50	11.6	11.2	8.3	9.1	2.0	0
$C_5H_5Fe^+$	15	3.0	0.4	0.7	0.7	2.3	2.1
	50	8.7	5.2	6.1	10.0	11.2	10.1
$C_5H_5FeH^+$	15	0.1	1.5	1.3[a]	0.2	0.2	0.2
	50	0.6	3.1	2.4	1.2	0.5	0.2
$C_5H_5FeC_5H_5^+$	15	0.5	2.2	4.1	5.9	6.3	4.7
	50	0.2	0.7	4.0	2.9	2.0	1.9

[a] The ions $[P-C_5H_5D]^+$ and $[CpFeD]^+$ are absent from the spectrum.

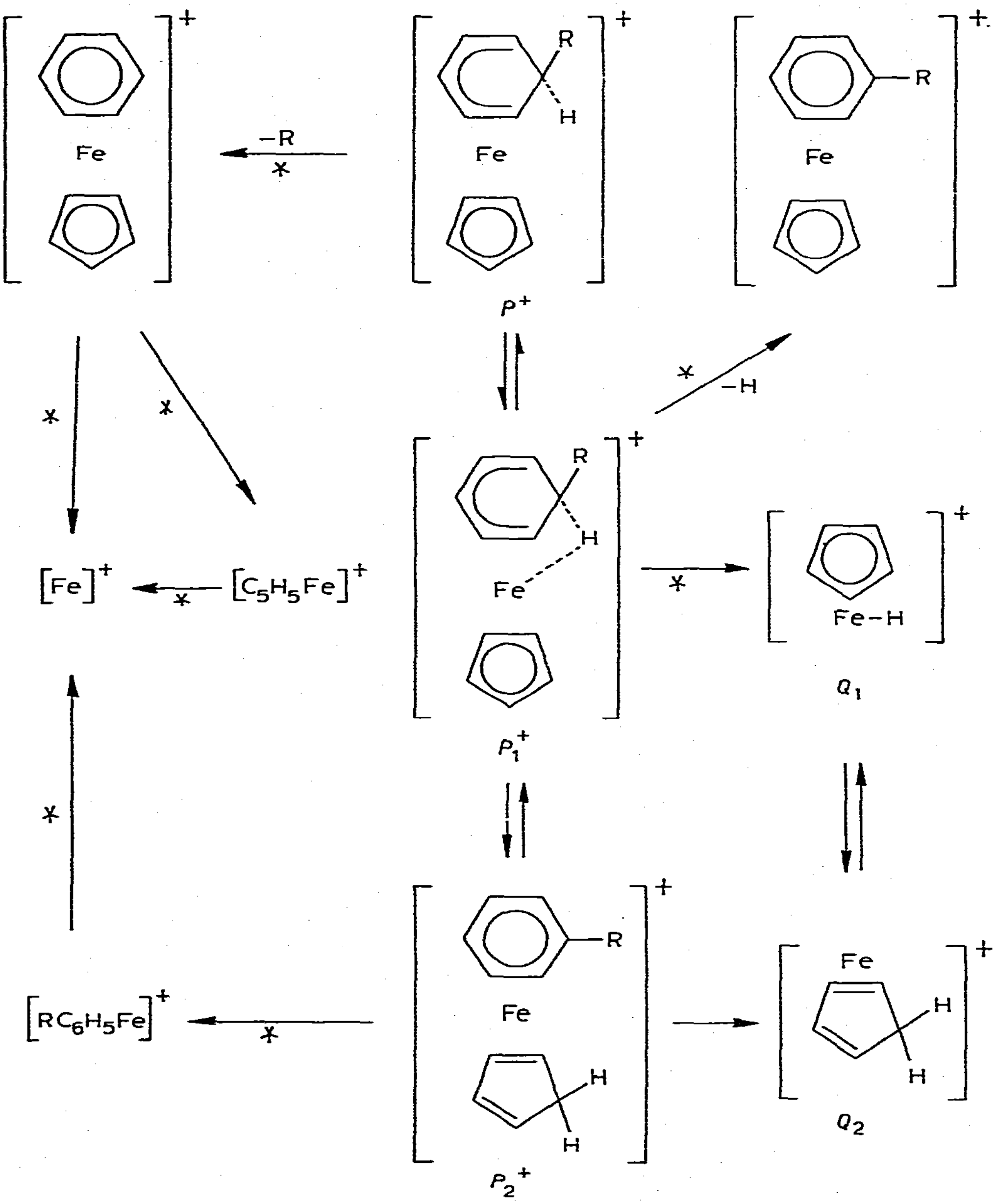
lyzed to show that dehydrogenation of the molecular ions is stereoselective and involves the *endo*-hydrogen atoms.

To shed more light on the problem, we have studied the mass spectra of *exo*-R-derivatives of cyclohexadienyl(cyclopentadienyl)iron,

In the molecular ion $[P]^+$ of the unsubstituted complex I, the hydrogen elimination is practically selective and comprises just the *endo*-atom elimination, as verified by a study of the *exo*-D-analogue (see ref. 2 and the present results). Fragmentation of the *exo*-complexes (III-VI), in contrast, involves both *endo*-H and *exo*-R abstractions and thus proceeds via two competing routes which depend on the nature of R. The $[P-R]^+$ contribution increases with the hydrocarbon chain length and decreases in going from alkyl substituents to phenyl (Table 1). The manner and degree of molecular ion fragmentation are known to depend on the energy of the cleaving bonds and stability of the resulting (charged or neutral) fragments. Consequently, the fact that the *endo*-H elimination becomes less stereoselective when the *exo*-hydrogen is substituted by a hydrocarbon group may be explained by assuming that the C—C bond dissociation energy is lower than the C—H bond energy while alkyl groups are more stable than the hydrogen atom and, probably, the ions $[C_6H_6FeC_5H_5]^+$ are more stable than $[RC_6H_5FeC_5H_5]^+$.

The stereoselectivity in the cyclohexadienyl(cyclopentadienyl)iron *exo*-D-analogue (II) has been explained [2] in terms of the iron participating in the process. The *endo*-H elimination was assumed to occur via the migration to the iron followed by the Fe—H bond rupture. This agrees with the ions $[C_5H_5FeH]^+$ (*m/e* 122) found in the spectra of the π-complexes I-VI studied. Formation of these ions is absolutely stereoselective and involves the *endo*-hydrogens only, as verified by the absence of the ions $[C_5H_5FeR]^+$ in the spectra and the presence of $[C_5H_5FeD]^+$ formed as a result of *exo*-R migration in the *exo*-D derivative (II).

SCHEME 1.



Another route of stereoselective fragmentation observed in all the complexes studied is elimination of a cyclopentadienyl molecule, C_5H_6, resulting in $[RC_6H_5Fe]^+$. For I and its *exo*-D-analogue II it was assumed [2] that the ions $[RC_6H_5Fe]^+$ ($R = H, D$) arose from the respective ions $[RC_6H_5FeC_5H_5]^+$ ($[P - H]^+$) through a loss of C_5H_5. However, no $[C_6H_6Fe]^+$ ions (*m/e* 134) have been found in the spectra of the substituted complexes III-IV although the ions $[C_6H_6FeC_5H_5]^+$ do have high intensities (Table 1). At the same time the $[C_6H_6Fe]^+$ intensity is extremely low

TABLE 2

METASTABLE TRANSITIONS IN MASS SPECTRA OF *endo*-R-SUBSTITUTED CYCLOHEXADIENYL-(CYCLOPENTADIENYL)IRON DERIVATIVES

Metastable transition source		Found m^*	Calcd. m^*
II	$[RC_6H_6FeC_5H_5]^+ \to [RC_6H_5FeC_5H_5]^+ + H$	199.0	199.0
III	$[RC_6H_6FeC_5H_5]^+ \to [C_6H_6FeC_5H_5]^+ + R^·$	185.0	185.0
IV		173.8	173.7
V		143.5	143.5
I	$[RC_6H_6FeC_5H_5]^+ \to [RC_6H_5Fe]^+ + C_5H_6$	89.5	89.7
III		102.0	102.3
II	$[RC_6H_6FeC_5H_5]^+ \to [C_5H_5FeH]^+ + RC_6H_5$	74.0	74.0
III		69.5	69.6
IV		65.0	65.2
V		53.8	53.8
VI		47.1	47.1
III	$[RC_6H_6FeC_5H_5]^+ \to [C_5H_5Fe]^+ + RC_6H_6$	68.5	68.4
IV		64.0	64.2

in the spectrum of π-benzene(cyclopentadienyl)iron $C_6H_6FeC_5H_5$ [7]. Consequently, it is not so probable that the ions $[RC_6H_5Fe]^+$ form via C_5H_5 elimination from $[P-H]^+$. The ions may be assumed to form predominantly from the $[P-C_5H_6]^+$ ion. This agrees with metastable peaks found in the spectra (Table 2). The process, related to the hydrogen atom migration from the cyclohexadienyl ring to the cyclopentadienyl, is rigorously selective and involves just the *endo*-hydrogen, since no $[C_6H_6Fe]^+$ ions formed by the *exo*-R migration and C_5H_5R elimination have been found with any of the *exo*-R-complexes.

The C_5H_5 elimination source is, probably, an isomeric molecular ion, benzene(cyclopentadienyl)iron, $[P_2]^+$. The latter species is formed via stereoselective migration of the cyclopentadienyl *endo*-H-atom to the iron (Scheme 1). Another possibility is that part, if not all, of the ions of *m/e* 122 arise from the isomeric molecular ion. The resulting ions $[C_5H_6Fe]^+$ (*m/e* 122) should have cyclopentadienyliron (Q_2) structures.

To sum up, the main fragmentation route in π-cyclohexadienyl(cyclopentadienyl)iron derivatives is a stereoselective migration of the *endo*-hydrogen of the cyclohexadienyl ring to the iron.

Experimental

Mass spectra were run on an MKh-1303 spectrometer fitted with a direct inlet system, ionising voltage was 50 and 15 eV, emission current was 1 mA, the inlet system temperature was 5 to 90°C, the ionising chamber temperature was 150°C.

The synthesis of the complexes $RC_6H_6FeC_5H_5$ (R = H, CH_3, C_2H_5, C_6H_5 or CCl_3) is described elsewhere [7-8]. The *exo*-deuteriated $DC_6H_6FeC_5H_5$ was obtained by treating $(C_6H_6FeC_5H_5)BF_4$ (0.1 g, 5 mmol) with $LiAlD_4$ (0.1 g, 2.5 mmol) in dimethoxyethane. The yield was 50%, m.p. 138-140°C after recrystallisation from pentane. (Found: C, 65.91, 66.07; H, 6.31, 6.32; Fe, 27.27, 27.46. $C_{11}H_{11}DFe$ calcd.: C, 65.72; H, 6.51; Fe, 27.78%.)

An IR spectrum of $DC_6H_6FeC_5H_5$ contains no band at 2750 to 2800 cm^{-1} (*exo*-deuterium).

A PMR spectrum (Hitachi—Perkin—Elmer R-20, 60 MHz, CS_2, 34°C) contains no highfield (δ 1.35 ppm) *exo*-H signal, while the lower-field signal is a triplet at δ 2.33 ppm (*endo*-H). The other protons are assigned as follows: δ 5.96 (H1), 4.12 (H2.6), 1.91 (H3.5), 4.13 ppm (C_5H_5).

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