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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XII *. FERROCENYL AND CYMANTRENYL DERIVATIVES OF CHALCONES

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Summary

The main processes of the electron-impact induced fragmentation of the ferrocenyl and cymantrenyl analogues of chalcones RCOCH=CHR′ (R, R′ = C_5H_4-FeC_5H_5, $C_5H_4Mn(CO)_3$, or aryl) involve a cleavage of the metal—ligand bond. A "chalcone" mode of fragmentation is weakly pronounced, due to the fact that the positive charge is localized preferably on the metal atom.

At present it is commonly accepted [2] that in molecular ions of π-complexes the positive charge is preferably localized on the transition metal atom thus conditioning the pathways of their fragmentation under the electron-impact. Replacement of the chalcone phenyl group by ferrocenyl or cymantrenyl may result in competition for the charge between the aromatic and the metal-containing fragments of the molecule. This in turn should be reflected in the mass spectral behaviour of these compounds. With the aim to investigate the effect of the cyclopentadienyl group π-bonded to the transition metal atom, on the chalcone fragmentation, as well as the effect of the ArCH=CHCO and ArCOCH=CH substituents on the fragmentation of the organometallic moiety, we have studied the mass spectra of the organometallic analogues of chalcone (I—VIII).

The mass spectra of several ferrocenyl analogues of chalcone were earlier reported in the literature, though without interpretation (FcCH=CHCOC_6H_5 ** [3], FcCOCH=C(CH_3)Fc [4], FcCOCH=CHX and FcCH=CHCOX [5], X denotes substituted or non-substituted α-furyl group).

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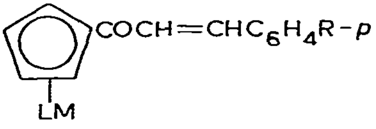
* For part XI see ref. [1].

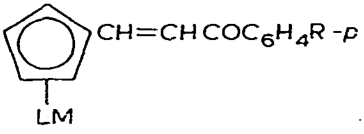
** Fc = $C_5H_5FeC_5H_4$, ferrocenyl.



(I, LM = C_5H_5Fe, R = H;
II, LM = C_5H_5Fe, R = Br;
III, LM = C_5H_5Fe, R = OCH_3;
IV, LM = $(CO)_3Mn$, R = H)

(I-IV)

The mass spectra of the ferrocenyl derivatives I—III and V—VII show strong (base for I—III) molecular ions (P^+) whose stability, as determined by the ratio of their intensities to the sum of the intensities at all the ions ($W = [P^+]/[\Sigma\phi_i^+] + [P^+]$), lowers in going from the acyl derivatives of ferrocene * (I—III) to the corresponding isomeric vinyl derivatives (V—VII) ($W_{C=O}/W_{CH=CH} > 1$, see Table 1). Apparently this fact can be attributed to interaction of the trivalent iron atom with the electro-negative oxygen atom of the α-carbonyl group. The argument in favour of this assumption is an appreciable increase in the contribution of the molecular ion in mass spectrum, observed in going from I, II to III, which is due to a donor effect of the methoxy substituents, leading to an increase in the electron density on the carbonyl oxygen atom.



(V, LM = C_5H_5Fe, R = H;
VI, LM = C_5H_5Fe, R = Br;
VII, LM = C_5H_5Fe, R = OCH_3;
VIII, LM = $(CO)_3Mn$, R = H)

(V-VIII)

The most intense fragment ions, $(P - C_5H_5)^+$, $C_5H_5Fe^+$ and Fe^+, in the mass spectra of I—III and V—VII result from cleavage of the metal—ligand bonds (fragmentation of the "ferrocenyl" mode). In this case the ratio $Z = [P - C_5H_5^+]/[C_5H_5Fe^+]$ for the acyl derivatives I—III is considerably lower than that for the vinyl analogues V—VII ($Z_{C=O}$ = 0.7—0.9, $Z_{CH=CH}$ = 7—11). These data agree well with similar quantities for the simplest acylferrocenes (for $FcCOCH_3$ $Z_{C=O}$ = 0.25 [5], 0.31 [6]) and vinylferrocenes (for FcCH= CHCOR $Z_{CH=CH}$ = 1.4—5.5 [7]). That the ions $(P - C_5H_5)^+$ predominate over the ions $C_5H_5Fe^+$ in the mass spectra of the vinyl analogues seems to be due to interaction of the double bond of the ion $C_6H_5COCH{=}CHC_5H_4Fe^+$ with the coordinatively unsaturated iron atom, which brings about an additional stabilization of this ion. In the molecular ion where the central iron atom is coordinatively saturated, such a stabilization mechanism does not occur.

The other fragmentation pathway, characteristic of α-carbonyl transition metal π-complexes such as LML'COR, is a migration of the R group to the metal, followed by formation of the LMR^+ or MR^+ ions [6]. This process proceeds in the mass spectra of the acyl derivatives I—III only and yields the ions $C_5H_5FeCH{=}CHAr^+$ and $FeCH{=}CHAr^+$. The cleavage of the δ-C—C bond (in respect to the C_5H_4 ring) gives rise to the ions $C_6H_5Fe^+$ in the mass spectrum of I and its isomer V.

A comparison of the mass spectra of chalcone and its ferrocenyl analogue

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* By the "acyl (vinyl) derivatives of ferrocene" will be implied compounds containing the carbonyl (vinyl) group bound to the ferrocenyl nucleus.

TABLE 1

THE MASS SPECTRA OF FERROCENYL (I—III, V—III) AND CYMANTRENYL (IV, VIII) ANALOGUES OF CHALCONES

Ion	I	II	III	IV	V	VI	VII	VIII
P^+	26.2	45.9	57.9	00.35	23.7	34.2	27.3	0.30
$P-L^{+}$[a]	10.0	4.7	6.9	20.8	33.9	32.0	32.0	17.7
LM^+	14.9	6.0	7.7	—	4.4	3.0	4.5	—
M^+	8.6	5.1	5.1	25.0	6.1	3.3	4.5	44.2
$LMC_5H_4C{\equiv}CH^+$	—	—	—	—	0.7	0.2	0.5	—
$MC_5H_4C{\equiv}CH^+$	—	—	—	—	3.4	1.2	0.9	2.2
$MCH{=}CHC_6H_4R^+$	1.0	0.6	—	15.3	—	—	—	—
$MC_6H_4R^+$	4.2	—	1.3	4.8	2.0	—	—	7.1
$FcCO^+$	0.2	0.5	—	—	—	—	—	—
Fc^+	2.1	0.9	0.4	—	—	—	—	—
$RC_6H_4CH{=}CH^+$	3.7	4.5 [b]	2.1	4.0	—	—	—	—
$RC_6H_4CO^+$	—	—	—	—	1.7	0.4	2.3	3.1
$RC_6H_4^+$	5.0	—	—	2.8	4.4	1.1	0.4	8.0
$P-CO^+$	0.8	0.2	—	—	—	—	—	—
$P-L-CO^+$	2.1	—	0.3	—	0.7	—	—	—
$P-L-COC_2H_2^+$	—	—	—	—	3.0	—	0.3	—
$P-LM^+$	—	—	—	0.5	—	—	—	0.4
$P-L-C_6H_5R^+$	—	—	1.3	—	0.4	—	—	0.4
FcH^+	1.8	1.5	2.6	—	—	—	0.5	—
MnH^+			2.2					9.3
$C_{13}H_9M^+$	0.2	1.8	—	1.7	1.7	0.3	—	—
$C_{13}H_9^+$	4.2	9.6	1.3	2.8	8.1	10.7	1.5	2.7
$W_{P_{C=O}}/W_{P_{CH=CH}}$	1.1	1.3	2.1	1.2				
ΣM^+	64	63	95	86	77	81	90	83
$P-L^+/LM^+$	0.67	0.78	0.9		7.7	10.7	7.1	

[a] $L = C_5H_5$ for $M = Fe$ and $L = (CO)_3$ for $M = Mn$. [b] For the $C_6H_4C_2H_2^+$ ion.

shows that replacement of the phenyl group by ferrocenyl reduces appreciably the contribution of the "chalcone" mode of fragmentation. For chalcones Ar′CH=CHCOAr″ [9—11] the main destruction pathways involve elimination of the hydrogen atom, cleavage of the CH—CO bond (yielding the ions $Ar'C_2H_2^+$ and $Ar''CO^+$), and loss of Ar″, Ar′H or CO groups from the molecular ion or formation of Ar^+ ions. In the ferrocenyl analogues of chalcone these processes proceed only slightly to give fragment ions of low intensity: $FcCO^+$(for I, III), $ArC_2H_2^+$ (I—III), $ArCO^+$ (V—VII), and $P-CO^+$ (I, III) or $P-C_5H_5-CO^+$ (I, II, V). No $FeC_2H_2^+$ ions are observed in the mass spectra of V—VII. Instead of these, the rearrangement ions FcC_2H^+ and $FeC_5H_4C_2H^+$ are present. Such a change in properties of the aromatic system, caused by introducing the organometallic group, can well be interpreted in terms of localization of the positive charge in the metal atom [12]. This change is due to the fact that in the odd-electron molecular ion of a free chalcone the "active" radical center is the driving force behind the radical elimination processes yielding stable even-electron ions. In particular, in organic compounds, the C—H bond is the strongest and elimination of the hydrogen atom from the odd-electron ion is usually followed by rearrangement affording a fresh bond, the energy realized therewith compensates for the energy consumed by cleavage of the C—H bond. Thus in the case of chalcone the loss of the hydrogen atom was supposed to be accompanied by cyclization yielding a stable even-electron ion [9].

Obviously, in the molecular ion of the π-complex, where the charge is localized on the metal and the ligand contains no "active" radical centre, such a process is disadvantageous. Indeed, none of the ferrocenyl analogues of chalcone (I—III and V—VII) studied up till now has displayed the $P - H^+$ ions. For the same reason simple cleavage of the ligand CO—CH bond, which would result in the ions $FcCO^+$ (for I—III) and $FcC_2H_2^+$ (for V—VII), proceeds only slightly, because the ions indicated were formally the odd-electron ions.

Thus, the localization of charge on the metal atom of π-complexes is a factor determining their fragmentation mode under electron impact. The aromatic group competes only slightly with the metal for having the charge. This is evident from a high value of the ratio between the total of the intensities of the metal-containing ions (ΣM^+) and that of all the ions in the mass spectra of I—III and V—VII (Table 1). (This ratio can be accepted as a measure of localization of charge on the metal atom.)

The "chalcone" mode of fragmentation occurs only in those molecular ions where the charge is localized on the aromatic fragment of the ion. Belonging to those are low intensity even-electron ions, e.g. $RC_6H_4CO^+$ (V—VIII) and $RC_6H_4C_2H_2^+$ (I—III).

The localization of charge on the metal conditions the fragmentation of cymantrenyl analogues of chalcone IV and VIII also (Table 1). The molecular ions of these compounds are of extremely low intensity and break down with loss of three carbonyl groups and the organic ligand to give the base ions Mn^+. As in the case of I—III, the migration of the $CH{=}CHC_6H_5$ group to the metal, yielding the ions $MnCH{=}CHC_6H_5^+$, is typical of the acyl analogue IV. Formation of the $MnC_6H_5^+$ ions is observed in the mass spectra of both the isomers IV and VIII.

The "chalcone" mode of fragmentation of the cymantrenyl derivatives IV and VIII is weakly pronounced. The ions $C_6H_5CO^+$ or $C_6H_5C_2H_2^+$ are of no more than 4% intensity, while the ions $(CO)_nMnC_5H_4CO^+$ or $(CO)_nMnC_5H_4C_2H_2^+$ (n = 0—3) are absent. Instead of the latter type the ions $MnC_5H_4C_2H^+$ occur in the mass spectrum of VIII. In complete analogy to the ferrocenyl derivatives, no elimination of the hydrogen or CO group from the ligand takes place in the ions $P - n(CO)^+$.

Experimental

The mass spectra were measured on an AEI MS-30/DS-50 mass spectrometer equipped with a direct inlet system. The operating conditions were: source temperature 200°C, ionizing energy 70 eV.

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