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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XX *. DIMETHYLAMINOALKYL DERIVATIVES OF FERROCENE AND CYMANTRENE; THE DETERMINATION OF THE DISTRIBUTION AND THE TOTAL CONTENT OF DEUTERIUM LABEL

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Summary

The mass spectrometry behaviour of dimethylaminomethyl- and α-(dimethylamino)ethyl derivatives of cymantrene and ferrocene, their iodine methylates as well as of the deutero analogues of these compounds has been studied. It has been shown that mass spectrometry can be successfully employed for the quantitative determination of the total deuterium content in aminoalkyl derivatives of cymantrene and ferrocene, the distribution of the label between the dimethylaminoalkyl group and the metallocenyl fragment and in case of the dimethylaminomethylferrocene also between the substituted and unsubstituted cyclopentadienyl rings. The data on the distribution of the isotopic label were used to ascertain the mechanism of fragmentation of the dimethylaminomethylferrocene under electron impact.

Introduction

Numerous investigations in organic and organoelement chemistry using compounds containing hydrogen isotopes are associated with the problem of quantitative and qualitative analysis of the content of deuterium in labelled compounds. Mass spectrometry is one of possible methods adopted to obtain information of this kind. In particular, this method has been employed [2] in studying the metallation of dimethylaminomethylcymantrene (I) with n-butyllithium, followed by treatment of the resulting organolithium compounds with deuterium oxide. This paper provides the data from a mass spectrometry investigation of dimethylaminoalkyl derivatives of cymantrene (I and II) and ferrocene (III and IV) and their deutero analogues prepared by the metallation reaction (see Exper-

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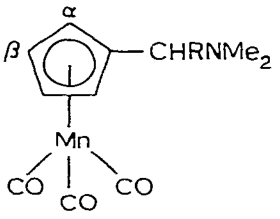
* For part XIX, see ref. 1.

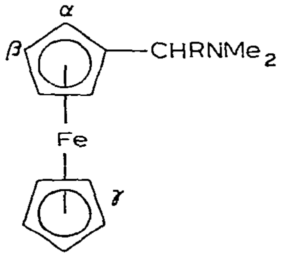
imental) with a view to determining the content and distribution of deuterium in these compounds.

Results and discussion

The possibility of applying mass spectroscopy to the isotope analysis is determined by the specific behaviour of the compound in a mass spectrometer. One of the limitations of the mass spectrometry method in carrying out isotope analysis of π-complexes of transition metals resides in the possibility of various secondary processes taking place in the mass spectrometer [3]. A study of the relationship of mass spectral characteristics of amines I—IV vs. temperature has shown that they are not subjected, except IV, to thermal decomposition in the mass spectrometer. In the case of IV a partial thermolysis with the formation of vinylferrocene is observed.



(I, R = H ; II R = Me)

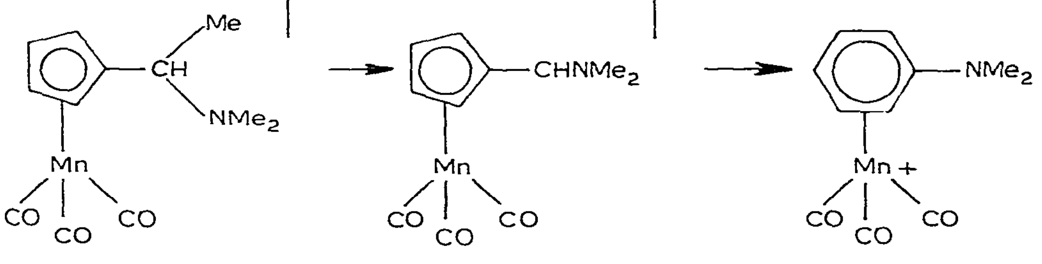


(III, R = H ; IV, R = Me)

In the combined evaporation of I—IV with D_2O in a mass spectrometer no protonated (hydrogenated) molecular or fragment ions or processes of exchange with hydrogen atoms are observed. Consequently, the possibility of isotope analysis of amines I—IV should be defined solely by the scheme of their fragmentation under electron impact.

The principal process of destruction of molecular ions (P^+) of I and II is the elimination of carbonyl ligands resulting in the formation of the ions $P^+ - n$CO (n = 1—3) (Fig. 1). An interesting feature of the fragmentation of amine II is the presence of ions $[(CO)_3MnC_5H_4CHNMe_2]^+$ and $[(CO)_3MnC_5H_4CHMe]^+$. These ions are stable particles in a mass spectrometer, which is probably due to their isomerization into a structure similar to the benzenetricarbonylmanganese cation [1], e.g. according to Scheme 1.

SCHEME 1



Fragmentation pathways for the ions $P^+ - 3$ CO differ from the pathways for the molecular ions P^+. The main process is the elimination of the molecule

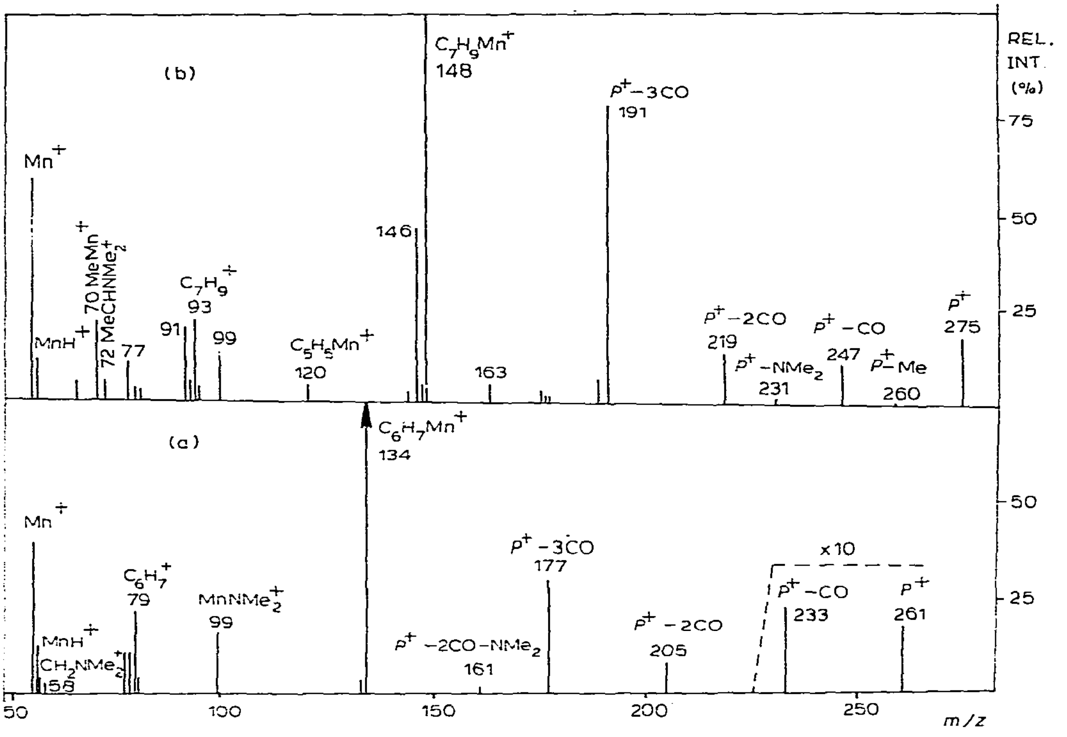


Fig. 1. Mass spectra (70 eV) of $Me_2NCH_2C_5H_4Mn(CO)_3$ (a) and $Me_2NCH(Me)C_5H_4Mn(CO)_3$ (b).

$MeN{=}CH_2$ with the formation of ions $[RCH_2C_5H_4Mn]^+$ (R = H or Me) *.

Simultaneously with this process, the metal—cyclopentadienyl ring bond in ions $P^+ - 3$ CO is broken thus giving ions Mn^+ or rearranged ions $MnNMe_2^+$ and MnR^+. In addition, in the mass spectra of I and II a number of ions containing no metal atom is present. One of the most intense among them is the ion Me_2NCHR^+.

Analysis of the mass spectra of III and IV (Fig. 2) indicated that for the molecular ions of these compounds substantially all destruction pathways known for ferrocene derivatives are realized. These include, first of all, reactions of metal—ligand bond cleavage resulting in ions $C_5H_5Fe^+$ (for III and IV) and $P^+ - C_5H_6$ (for III). In the spectrum of III the formation of the rearranged ions $C_5H_6Fe^+$, $P^+ - C_5H_6$ and $C_5H_5FeNMe_2^+$, and the ion $C_5H_6Fe^+$ in the case of IV, is also observed. In the spectrum of III the ions $C_{10}H_{10}Fe^+$ and $P^+ - MeN{=}CH_2$ have a high intensity. In the case of IV there is no loss of $MeN{=}CH_2$ from P^+ and the most intense ion is $P^+ - Me_2NH$ (the product of 1,2-elimination).

The common feature of the behaviour of the discussed compounds (I--IV) under electron impact is the easy formation of gas-phase ions of the type

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* In contrast to the data described in ref. 4, we have found that in the spectrum of I the most intense ion is $C_6H_7Mn^+$ with m/z of 134, and in the spectrum of its deutero analogue, $(CO)_3MnC_5H_3$-DCH_2NMe_2, the ion with m/z of 135; the intensity of the ion $C_6H_6Mn^+$ is 4% of that of m/z 134.

α-metallocenylcarbenium. The aminocarbenium ions $LMC_5H_4CHNMe_2^+$ (LM = $(CO)_3Mn$ or C_5H_5Fe) should be particularly noted, since their properties in the condensed phase are insufficiently studied.

The above-given analysis of the mass spectrometry behaviour of compounds I--IV has made it possible to come to certain conclusions as regards the feasibility of qualitative and quantitative analysis of their deutero analogues.

The presence of intense molecular ions, as well as ions $P^+ - n\,CO$ (n = 1, 2) in the mass spectra of cymantrenyl derivatives I and II makes it possible to establish the total content of the label. Furthermore, in the mass spectra of these compounds there is a sufficient amount of fragment ions to determine the content of deuterium in every structural unit (cyclopentadienyl, dimethylamino, methylene or ethylidene groups). Analysis of the isotope distribution for the ions $CHRNMe_2^+$, $MnNMe_2^+$ (II) in the mass spectra of the products of deutero exchange of I and II points to the absence of the label in the substituent. Consequently, the content of deuterium in the cyclopentadienyl ring in this case coincides with the total amount in the whole molecule and can be determined by the ions $P^+ - n\,CO$, wherein n = 0—2. The use of ions $P^+ - 3\,CO$ and $P^+ - 3\,CO{-}MeN{=}CH_2$ for the same purposes is impossible, since they are accompanied by fragments containing a lesser (by one or more) number of hydrogen atoms.

The determination of the total content of deuterium in IV can be also effected by analysis of the molecular ion group. However, in the case of amine

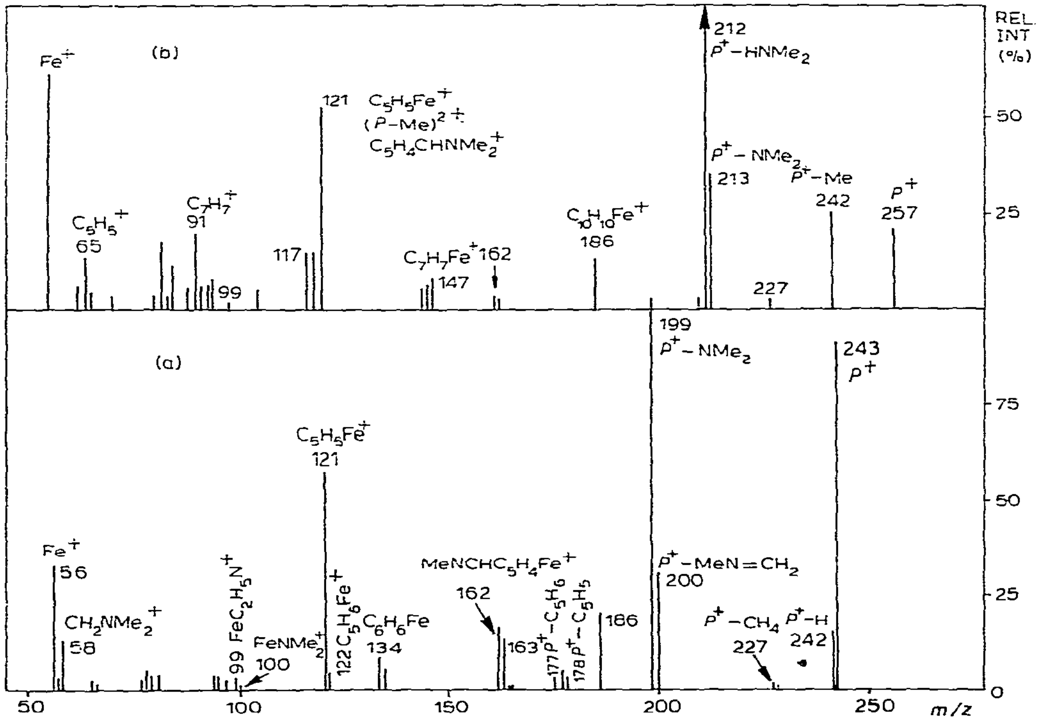


Fig. 2. Mass spectra (70 eV) of $Me_2NCH_2C_5H_4FeC_5H_5$ (a) and $Me_2NCH(Me)C_5H_4FeC_5H_5$ (b).

III the ions $P^+ - H$ and $P^+ - H_2$ are present and retain their high intensity even at low ionization energy (the ratio $[P^+ - H]/[P^+]$ is about 0.1 at 10 eV). Hence, isotope analysis of the molecular ion group in deutero analogues of III is impossible.

Another possible way of determining the total content of deuterium is the analysis of the fragment ions complementing each other to the complete structure of the starting compound. Among fragments meeting this requirement in the mass spectrum of III are $C_5H_5Fe^+$ and $FeC_5H_4CH_2NMe_2^+$, $C_5H_5FeNMe_2^+$ and $FeC_5H_4CH_2^+$ and the like. However, as is seen from Fig. 2, each of these ions is accompanied with fragments differing by one or more hydrogen atoms. Besides, it is also possible that the formation of some of these ions is preceded by a complete rearrangement of hydrogen atoms between the ligands, just as in the spectrum of methylferrocene [5]. Consequently, the use of these ions for the isotope analysis is not possible.

Nevertheless, the presence of the ions $C_{10}H_{10}Fe^+$ and $Me_2N{=}CH_2^+$ in the spectrum of III makes it possible to obtain information on the distribution of the label between the ferrocenyl radical and the substituent. In the spectra of deutero derivatives of III the value of the intensity ratio of the ions *m/z* 59 and *m/z* 58 does not exceed the natural isotope distribution for the composition C_3H_8N. This points to the absence of deuterium in the side chain and, hence, the total content of the tracer in deutero analogues of III can be determined from the consideration of the ions $C_{10}H_{10}Fe^+$.

Consequently, from the data from the mass spectra of free bases III and IV information can be obtained only for the total amount of the label or its distribution between the ferrocenyl residue and the substituent. Analysis of the distribution of deuterium between the cyclopentadienyl rings through the products of breakdown of the metal—ligand bonds becomes hindered, in particular due to the superposition of ions $C_5H_4DFe^+$ and $C_5H_6Fe^+$.

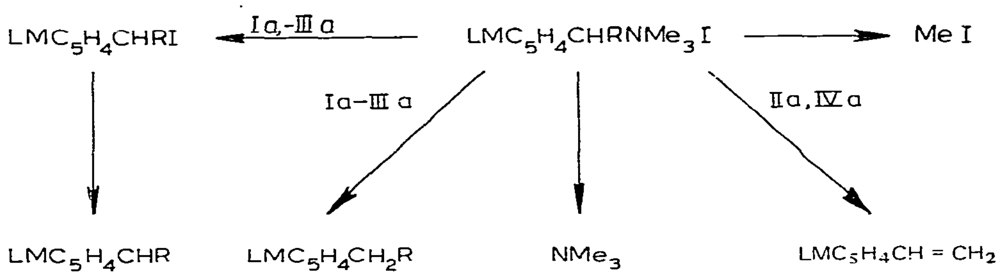
Among the techniques employed for interpretation of the mass spectrometry data is the preparation of chemical derivatives of the compound being studied. The most trivial derivatives of the amines I—IV are their iodine methylates: $(CO)_3MnC_5H_4CH_2NMe_3I$ (Ia), $(CO)_3MnC_5H_4CH(Me)NMe_3I$ (IIa), $C_5H_5FeC_5H_4CH_2NMe_3I$ (IIIa) and $C_5H_5FeC_5H_4CH(Me)NMe_3I$ (IVa).

In the mass spectra of Ia—IVa there are no ions containing, at the same time, atoms of a metal and nitrogen, or nitrogen and iodine. The ions observed in the spectra of these compounds are formed solely as a result of ionization and fragmentation of the products of their thermal decomposition (Scheme 2). The results of the isotope analysis of the ions $(CO)_3MnC_5H_4CHRI$ in the spectra of Ia and IIa coincide with the data obtained for the free amines.

Among the products of thermal decomposition of IIIa, iodinemethylferrocene $C_5H_5FeC_5H_4CH_2I$ is noteworthy. The molecular ion of this compound does not decompose with the loss of hydrogen atoms, thus making it possible to calculate the content of deuterium in the ferrocenylmethyl group.

The data obtained by this method can be confirmed by the analysis of ions $C_5H_5FeI^+$ and $FeC_5H_4CH_2I^+$ formed by fragmentation of the molecular ion of this compound (Table 1). In addition, the presence of the above-mentioned products of breakdown of the metal—ligand bond makes it possible to determine the content of deuterium in each of the cyclopentadienyl rings which

SCHEME 2



LM = $(CO)_3Mn$ for Ia and IIa, and C_5H_5Fe for IIIa, IVa; R is H or Me

characterizes the distribution of deuterium in molecules of III and IIIa.

Consequently, only the combined study of the mass spectra of III and its iodine methylate IIIa makes it possible to determine the amount of the label in the side chain and in every cyclopentadienyl ring. The absence of iodine-containing ions in the spectrum of IVa does not enable a similar analysis.

The data given in this paper on the content and distribution of deuterium in the products of metallation of I—III, formed by treatment of the corresponding organolithium compounds with deuterium oxide, are in full agreement with the results of a PMR investigation of these compounds (Table 2). Consequently, mass spectrometry can be successfully employed for the quantitative determination of the total content of deuterium in aminoalkyl derivatives of cymantrene and ferrocene, its distribution between the dimethylaminoalkyl group and the sandwich fragment and in some cases, for example for III, between the substituted and unsubstituted cyclopentadienyl rings.

The data on the distribution of the isotope label in deutero analogues of III or IIIa have been used by us to check the scheme of fragmentation of the free amine III. Just as in the case of methylferrocene [5], it could be assumed that the formation of certain fragments occurred after the redistribution of hydrogen atoms in the molecular ions. However, it is seen from Table 3 that calculation of the intensity of ions with *m/z* 121—124 and 134—137 for this case

TABLE 1

THE DISTRIBUTION OF THE LABEL IN THE DEUTERO ANALOGUES OF AMINE III

Structure element	Compound	Ion	d_0	d_1	d_2	d_3	d_4 [a]
C_5H_5	IIIa	$C_5H_5FeI^+$	55.4	38.8	5.8		
C_5H_4	IIIa	$C_5H_4CH_2FeI^+$	10.6	62.1	27.3		
	IIIa	(calculated) [b]	5.9	38.5	39.8	14.2	1.6
$C_5H_5FeC_5H_4$	IIIa	$C_{11}H_{11}FeI^+$	7.7	37.5	38.2	14.7	1.9
	III	$C_{10}H_{10}Fe^+$	9.2	36.8	35.7	15.7	2.5

[a] $d_i(\%) = (Id_i/\sum_i Id_i)100$, where Id_i is the intensity of the isotopic ion of given structure, with i being the number of deuterium atoms. [b] From the above data on the content of deuterium in $C_5H_5FeI^+$ and $C_5H_4CH_2FeI^+$ ions.

TABLE 2

THE DISTRIBUTION OF THE LABEL WITHIN THE MOLECULE OF MONODEUTEROAMINES I—III DERIVED FROM PMR [a] AND MASS SPECTRA (CONTENT OF D IN PARTS PER ATOM)

Amine	Method	Label position [b]		
		α	β	γ
I	PMR	0.97	0.10	—
	MS	1.11		—
II	PMR	0.86	0.14	—
	MS	0.95		—
III	PMR	0.79	0	0.21
	MS	0.72		0.26

[a] Eu(fod)3 or Dy(fod)3 was used to obtaine the resolved spectra of the cyclopentadienyl protons and the assignment of the signals. [b] No deutero label was found in the dimethylaminoalkyl group.

TABLE 3

THE EXPERIMENTAL AND CALCULATED MASS SPECTRUM OF THE DEUTERO ANALOGUE OF AMINE III (FOR THE SAMPLE MENTIONED IN TABLE 1)

Ion groups analysed	m/z	Relative intensity of peaks within the analysed group of ions		
		Experiment	Calculated	
			Mechanism A	Mechanism B
$C_5H_{5-n}D_nFe^+$ and $C_5H_{6-m}D_mFe^+$ [a]	121	45.3	33.2	47.5
	122	40.6	47.1	43.2
	123	11.2	16.4	8.8
	124	2.8	3.0	0.5
	125	—	(0.3)	—
$C_6H_{6-n}D_nFe^+$ and $C_6H_{7-m}D_mFe^+$	134	7.9	23.5	8.8
	135	38.0	39.3	40.4
	136	41.2	24.4	39.7
	137	12.9	10.6	11.1
	138	—	(2.2)	—
$C_{10}H_{10-n}D_nFe^+$	186	9.2	5.9	
	187	36.8	38.5	
	188	35.7	39.8	
	189	15.7	14.2	
	190	2.5	1.6	
$C_{11}H_{11-n}D_nFe^+$ and $C_{11}H_{12-m}D_mFe^+$	199	7.0	6.0	
	200	33.4	33.2	
	201	37.2	38.0	
	202	17.5	18.8	
	203	4.7	3.8	
	204	0.3	0.3	
$C_{13}H_{17-n}D_nFe^+$ and $C_{13}H_{16-m}D_mFe^+$ [a]	242	3.3	1.6	1.1
	243	14.4	12.8	11.7
	244	34.5	37.6	37.8
	245	30.8	34.5	34.6
	246	14.5	13.4	13.4
	247	2.5	1.3	1.5

[a] These ions are assumed to be formed via migration of methylene hydrogen.

(mechanism A; only the hydrogen atoms of the ferrocenylmethyl group are taken into account) does not meet the experimental data. A good agreement with the experiment is obtained by assuming that the hydrogen atoms of the ferrocenyl fragment keep their place on fragmentation (mechanism B). In particular, the formation of ions $C_5H_5FeH^+$ occurs due to the irreversible migration of the hydrogen atom from the α-methylene unit to the Fe atom.

In the above-described study of the mechanisms of fragmentation of III we have used its deutero analogues or their iodine methylates containing the deutero label in both cyclopentadienyl ligands. It enables us to conclude that for the determination of the scheme of destruction of certain compounds there is no need for labour-consuming syntheses of their selectively label-marked derivatives.

Experimental

The amines I, II, III and IV were prepared according to refs. 2, 8, 9 and 10, respectively. The quaternary salts of IIa, IIIa and IVa were prepared by methylation of amines II—IV [8,9,10]. In a similar manner, Ia with m.p. 236—237°C was isolated from amine I and MeI in acetone. Elemental analysis: found: C, 36.17; H, 3.89; Mn, 13.75, $C_{12}H_{15}NO_3MnI$, calcd: C, 35.75; H, 3.75; Mn, 13.63%.

Monodeutero analogues of amines I—III were prepared by metallation of these amines with an ethereal solution of n-BuLi in ether-THF (1 : 2) at —70°C (for I and II) and 24°C (for III) followed by treatment of the reaction mixture with D_2O [2]. The amines I—III, containing more than one D atom per molecule, were prepared by repeated metallation of the monodeuteroamines under similar conditions. All the deuterium-marked amines were converted into the corresponding iodine methylates as described above.

The following main ion peaks were observed in the mass spectra. Compound Ia (*m/z* (ion composition)): 344 ($[(CO)_3MnC_5H_4CH_2I]^+$), 309 (MnI_2^+), 260 ($MnC_5H_4CH_2I^+$), 233 ($[(CO)_2MnC_5H_4CH_2NMe_2]^+$), 218 ($[(CO)_3MnC_5H_4CH_3]^+$), 205 ($C_5H_4CH_2I^+$), 190 ($[(CO)_2MnC_5H_4CH_3]^+$), 182 ($MnI^+$), 177 ($MnC_5H_4CH_2$-$NMe_2^+$), 161 ($[(CO)MnC_5H_4CH_2]^+$), 142 ($MeI^+$), 134 ($MnC_5H_4CH_3^+$), 128 ($HI^+$), 127 ($I^+$), 59 ($NMe_3^+$), 58 ($NC_3H_8$), 57 ($NC_3H_7^+$), 55 ($Mn^+$).
Compound IIa: 358 ($[(CO)_3MnC_5H_4CHIMe]^+$), 281 (?), 274 ($MnC_5H_4CHIMe^+$), 230 ($[(CO)_3MnC_5H_4CHCH_2]^+$), 202 ($[(CO)_2MnC_5H_4CHCH_2]^+$), 191 (?), 182 (MnI^+), 174 ($[(CO)MnC_5H_4CHCH_2]^+$), 146 ($MnC_5H_4CHCH_2^+$), 128 (HI^+), 127 (I^+), 120 ($MnC_5H_5^+$), 91 ($C_7H_7^+$), 59 (NMe_3^+), 58 ($NC_3H_8^+$), 57 ($NC_3H_7^+$), 55 (Mn^+). Compound IIIa: 326 ($FcCH_2I]^+$), 261 ($FeC_5H_4CH_2I^+$), 248 ($C_5H_5FeI^+$), 200 ($FcMe^+$), 199 ($FcCH_2^+$), 186 (FcH^+), 183 (FeI^+), 142 (MeI^+), 134 ($C_6H_6Fe^+$), 128 (HI^+), 127 (I^+), 121 ($C_5H_5Fe^+$), 99.5 ($FcCH_2^{2+}$), 78 ($C_6H_6^+$), 59 (NMe_3^+), 58 ($NC_3H_8^+$), 57 ($NC_3H_7^+$), 56 (Fe^+).
Compound IVa: 424 ($[(FcC_2H_3]_2^+$), 282 (?), 257 ($FcCHMeNMe_2^+$), 236 (?), 212 ($FcC_2H_3^+$), 186 (FcH^+), 147 ($C_7H_7Fe^+$), 134 ($C_6H_6Fe^+$), 129 ($C_{10}H_9^+$), 128 (HI^+), 127 (I^+), 121 ($C_5H_5Fe^+$), 59 (NMe_3^+), 58 ($NC_3H_8^+$), 57 ($NC_3H_7^+$), 56 (Fe^+).

The mass spectra were obtained on a MS-30 mass spectrometer with a DS-50 data processing system at ionizing voltages of 70, 12 and 10 V and ionization chamber temperature of 200—250°C. The temperature of the direct input system in the case of I—IV is 25°C. The spectra Ia, IIa, IIIa and IVa were obtained at 280, 230, 200 and 150°C, respectively. The calculation of monoisotope spectra were performed using programs AELITA and ISOMETA [6,7]. PMR spectra were recorded on an R-12 instrument (Perkin-Elmer).

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