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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XI *. MANGANESE AND RHENIUM VINYLIDENE COMPLEXES

V.F. SIZOI *, YU.S. NEKRASOV, YU.N. SUKHAREV, N.E. KOLOBOVA,
O.M. KHITROVA, N.S. OBEZYUK and A.B. ANTONOVA

Institute of Organo-Element Compounds of the USSR Academy of Sciences, Vavilova 28, Moscow 117312 (U.S.S.R.)

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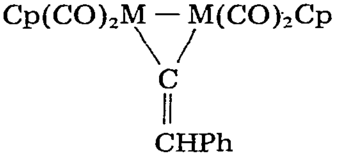
Summary

The mass spectra of $(\pi\text{-}C_5H_5)_nM_n(CO)(L)_1(L')$ (M = Mn, Re; L = CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$; L′ is a vinylidene ligand) are reported and characterised by strong dehydrogenation of the rhenium complexes. In bimetallic analogues, the Re—Re bond is stronger than the Mn—Mn.

Fragmentation of Mn- and Re-(cyclopentadienyl)carbonyl complexes containing CO and PX_3 ligands has been studied earlier [2—4].

We have studied the mass spectra of Mn- and Re-cyclopentadienyl complexes containing vinylidene ligands, including monometallic complexes $CpMn(CO)_2$-(C=CHPh) ** (I), $CpRe(CO)_2$(C=CHPh) (II), CpMn(CO)(PPh_3)(C = CHPh) (III), CpMn(CO)[P(OPh)$_3$](C=CHPh) (IV) and bimetallic complexes (V—VIII) [5—7].



(V, M = Mn) (VI, M = Re)

$Cp(CO)_2Mn(C_{16}H_{10})Mn(CO)_2Cp$

(VII)

$Cp(CO)_2Re[C{=}C(Ph)C(Ph){=}CH_2]Re(CO)_2Cp$

(VIII)

Compounds II, VI and VIII contain the polyisotopic element Re (the stable isotopes are ^{185}Re and ^{187}Re having relative abundances 0.3707 and 0.6293, respectively [8]). The presence of polyisotopic elements considerably complicates the quantitative interpretation of mass spectra because it bars a direct comparison of intensities of ions containing different numbers of atoms of the poly-

(*continued on p. 174*)

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* For part X see ref. 1.

** Cp = π-cyclopentadienyl and Ph = phenyl throughout the paper.

TABLE 1

MASS SPECTRUM OF $CpMn(CO)_2(C{=}CHPh)$ (I) (T_i = 45°C)

Ion	m/e	Relative intensity	Metastable ions	
			m/e	Transition
P^+	278	6	177.2	278 → 222 + 2CO
$P - CO^+$	250	0.3	64.9	222 → 120 + C_8H_6
$CpMnC_8H_6^+$	222	32	25.2	120 → 55 + C_5H_5
$C_8H_5Mn^+$	156	1		
$C_5H_5Mn^+$	120	100		
$C_8H_6^+$	102	9		
$C_6H_4^+$	76	3		
Mn^+	55	40		

TABLE 2

MASS SPECTRUM OF $CpRe(CO)_2(C{=}CHPh)$ (II) (T_i = 140°C)

Ion	m/e	Relative intensity	Ion	m/e	Relative intensity
P^+	410	23	$C_7H_3Re^+$	274	4
$P - CO^+$	382	28	$C_7H_2Re^+$	273	1
$P - 2CO^+$	354	100	C_7HRe^+	272	1
$P - 2CO - H_2^+$	352	5	$C_5H_5Re^+$	252	4
$P - 2CO - 2H_2^+$	350	6	$C_5H_3Re^+$	250	6
$C_3H_3Re(C_8H_6)^+$	328	23	$C_5H_2Re^+$	249	5
$C_{11}H_7Re^+$	326	8	C_5HRe^+	248	5
$C_{11}H_5Re^+$	324	7	$C_3H_3Re^+$	226	2
$CHReC_8H_6^+$	302	13	$C_3H_2Re^+$	225	6
$C_9H_5Re^+$	300	7	C_3HRe^+	224	7
$C_7H_7Re^+$	278	4	$CHRe^+$	200	3
$C_7H_5Re^+$	276	3	Re^+	187	8
$C_7H_4Re^+$	275	5	$C_8H_6^+$	102	2

TABLE 3

MASS SPECTRUM OF $CpMn(CO)(PPh)_3(C{=}CHPh)$ (III) (T_i = 40°C)

Ion	m/e	Relative intensity	Metastable ions	
			m/e	Transition
P^+	512	1.6	457.5	512 → 484 + CO
$P - CO^+$	484	8	301.5	484 → 382 + C_8H_6
$CpMnPPh_3^+$	382	100		
$Mn(PPh_2)C_6H_4^+$	316	2		
PPh_3^+	262	50		
$(C_6H_4)_2PMn^+$	238	3		
$CpMn(C{=}CHPh)^+$	222	2		
$CpMn(C_6H_4)^+$	196	7		
$C_{12}H_8P^+$	183	76		
$C_{12}H_8^+$	152	12		
$C_{11}H_9^+$	141	4		
$CpMn^+$	120	48		
PPh^+	108	40		
$C_8H_6^+$	102	36		
$C_5H_6^+$	66	32		
$C_5H_5^+$	65	20		
Mn^+	55	36		

TABLE 4

MASS SPECTRUM OF $CpMn(CO)[P(OPh)_3](C{=}CHPh)$ (IV)

Ion	*m/e*	Relative intensity	Ion	*m/e*	Relative intensity
P^+	560	2	$C_{12}H_9^+$	153	29
$P - CO^+$	532	5	$C_{12}H_8^+$	152	16
$CpMn[P(OPh)_3]^+$	430	26	$C_5H_5Mn^+$	120	32
$P(OPh)_3^+$	310	29	$C_8H_6^+$	102	87
$CpMnC_8H_6^+$	222	5	$PhOH^+$	94	22
$P(OPh)_2^+$	217	100	Ph^+	77	74
$CpMnOPh^+$	213	4	$C_5H_6^+$	66	76
$PhOPC_6H_4^+$	199	11	$C_5H_5^+$	65	41
$C_{12}H_{10}O_2^+$	186	11	Mn^+	55	14
$C_{12}H_9O_2^+$	185	8	$C_4H_3^+$	51	20
Ph_2O^+	170	8			

TABLE 5

MASS SPECTRUM OF $CpMn(CO)_2(C_8H_6)Mn(CO)_2Cp$ (V) (T_i = 105°C)

Ion	*m/e*	Relative intensity	Ion	*m/e*	Relative intensity
P^+	454	0.03	$CpMn(CO)_2^+$	176	8
$P - CO^+$	426	0.05	$CpMn(CO)^+$	148	27
$P - 2CO^+$	398	0.16	$CpMn^+$	120	100
$P - 4CO^+$	342	0.3	$C_8H_6^+$	102	10
$Cp_2Mn_2(CO)_3^+$	324	0.3	$C_3H_2Mn^+$	93	6
$Cp_2Mn_2^+$	240	0.7	C_2HMn^+	80	5
$CpMn_2(CO)_2^+$	231	0.2	$C_5H_6^+$	66	16
$CpMnC_8H_6^+$	222	1.5	$C_5H_5^+$	65	9
$CpMn(CO)_3^+$	204	19	Mn^+	55	88

TABLE 6

MASS SPECTRUM OF $CpRe(CO)_2(C_8H_6)Re(CO)_2Cp$ (VI) (T_i = 110°C)

Ion	*m/e*	Relative intensity	Ion	*m/e*	Relative intensity
P^+	716	32	$C_{16}H_8Re_2^+$	572	10
$P - CO^+$	688	7	$C_{14}H_{10}Re_2^+$	550	2
$P - 2CO^+$	660	14	$C_{14}H_8Re_2^+$	548	11
$P - 3CO^+$	632	34	$C_{12}H_8Re_2^+$	524	8
$P - 4CO^+$	604	100	$C_{10}H_8Re_2^+$	500	9
$P - 4CO - H_2^+$	602	16	$C_8H_6Re_2^+$	474	7
$P - 4CO - 2H_2^+$	600	11	$CpRe(CO)C_8H_6^+$	382	33
$P - 4CO - 3H_2^+$	598	25	$CpRe(C_8H_6)^+$	354	96
$C_{16}H_{12}Re_2^+$	576	6	$M - 4CO^{++}$	302	20
$C_{16}H_{10}Re_2^+$	574	14			

TABLE 7

MASS SPECTRUM OF $CpMn(CO)_2(C_{16}H_{10})Mn(CO)_2Cp$ (VII) (T_i = 190°C)

Ion	*m/e*	Relative intensity	Ion	*m/e*	Relative intensity
P^+	554	15	$CpMn(CO)_3^+$	204	100
$P - 2CO^+$	498	32	$C_{16}H_{10}^+$	202	6
$P - 4CO^+$	442	66	$Ph_2C_2^+$	178	29
$CpMn(CO)_2(C_{16}H_{10})^+$	378	15	$CpMn(CO)_2^+$	176	19
$P - 4CO - Cp^+$	377	24	$C_{12}H_6^+$	150	13
$CpMn(CO)(C_{16}H_{10})^+$	350	3	$CpMn(CO)^+$	148	16
$CpMn(C_{16}H_{10})^+$	322	78	$CpMn^+$	120	69
$CpMnC_8H_4^+$	275	16	$C_8H_6^+$	102	14
$Cp_2Mn_2^+$	240	8	Mn^+	55	32
$C_{13}H_9Mn^+$	220	8			

isotopic element. Moreover, the presence of one or more polyisotopic elements masks certain elimination processes such as elimination of hydrogen atoms and molecules.

In order to overcome these difficulties, the mass spectra of compounds II, VI and VIII have been transformed to the monoisotopic form using AÉLITA programme [9] (the mass spectra are listed in Tables 1—8). All the spectra contain rather intense molecular ions (P^+) and thus provide unambiguous assignments of molecular weights and compositions of the compounds studied.

The vinylidene complexes fragment in a rather simple way, following the usual pattern for cyclopentadienylmetalcarbonyls of consecutive elimination of the carbonyl groups to give the ions $P - n\ CO^+$, $CpML^+$ and M^+.

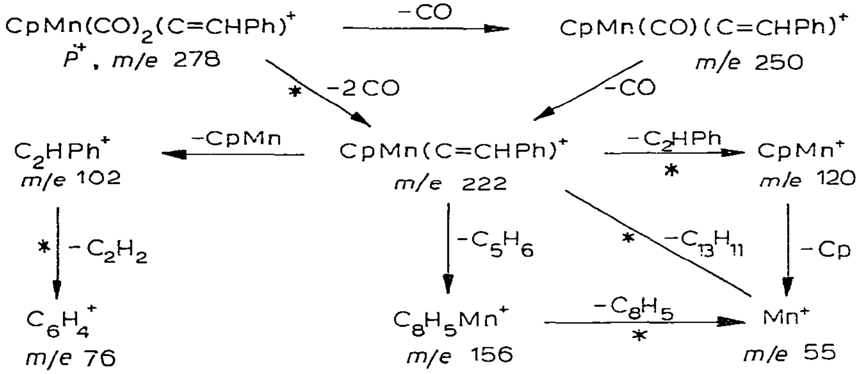
Fragmentation of $CpMn(CO)_2(C{=}CHPh)$(I) is shown in Scheme 1. The transitions proved by metastables are labelled with an asterisk. Consecutive (or sinchronous) elimination of both carbonyl ligands leads to the ion $CpMnC_8H_6^+$

TABLE 8

MASS SPECTRUM OF $CpRe(CO)_2(C_{16}H_{12}(Re(CO)_2Cp$ (VIII) (T_i = 190°C)

Ion	*m/e*	Relative intensity	Ion	*m/e*	Relative intensity
P^+	818	23	$C_{18}H_{12}Re_2^+$	600	4
$P - CO^+$	790	3	$C_{18}H_{10}Re_2^+$	598	4
$P - 2CO^+$	762	2	$C_{18}H_8Re_2^+$	596	3
$P - 3CO^+$	734	9	$CpRe(CO)_2C_{16}H_{12}^+$	512	50
$P - 4CO^+$	706	55	$C_{10}H_8Re_2^+$	500	9
$P - 4CO - H_2^+$	704	11	$CpRe(CO)C_{16}H_{12}^+$	484	9
$P - 4CO - 2H_2^+$	702	18	$CpReC_{16}H_{12}^+$	456	100
$P - 4CO - 3H_2^+$	700	9	$C_{21}H_{15}Re^+$	454	29
$P - 4CO - 4H_2^+$	698	4	$C_{21}H_{13}Re^+$	452	43
$P - 4CO - 5H_2^+$	696	5	$C_{21}H_{11}Re^+$	450	4
$C_{24}H_{18}Re_2^+$	678	3	$C_{21}H_9Re^+$	448	21
$C_{24}H_{16}Re_2^+$	676	1	$C_{19}H_{15}Re^+$	430	2
$C_{24}H_{14}Re_2^+$	674	6	$C_{19}H_{13}Re^+$	428	3
$C_{24}H_{12}Re_2^+$	672	1	$C_{19}H_{11}Re^+$	426	8
$C_{24}H_{10}Re_2^+$	670	4	$C_{19}H_9Re^+$	424	16
$C_{24}H_8Re_2^+$	668	1	$C_{19}H_7Re^+$	422	5
$C_{24}H_6Re_2^+$	666	2	$Re_2(CO)^+$	400	10
$C_{18}H_{16}Re_2^+$	604	5	Re_2^+	372	10

Schema 1. Fragmentation of $CpMn(CO)_2(C{=}CHPh)$ under electron impact.



which may further lose C_5H_5Mn, C_5H_6, $C_{13}H_{11}$ or C_8H_6 (the two latter processes have been proved by metastables). The replacement of one of the carbonyl groups in $CpMn(CO)_3$ (the mass spectrum, see Table 9) with the phenylvinylidene ligand greatly increases the extent of decarbonylation of the molecular ion. In fact, the $P - 2CO^+$ to P^+ ions intensity ratio is about unity in $CpMn(CO)_3$ while the $CpMn(C_8H_6)^+/P^+$ ratio in the mass spectrum of I amounts to 5.3. This may be due to the larger stability of the ion $CpMn(C_8H_6)^+$ compared with $CpMn(CO)^+$.

The introduction of PPh_3 or $P(OPh)_3$ into the molecule (see the mass spectra of III and IV) further increases the stabilities of the decarbonylation products, by a factor of 18 in the mass spectrum of III and by a factor of 9 in the mass spectrum of IV (with reference to the ion $M - 2\,CO^+$ in the mass spectrum of $CpMn(CO)_3$). Complexes III and IV both give rather intense free ligand ions PPh_3^+ and $P(OPh)_3^+$; the further fragmentations of these ions parallel those observed in the mass spectra of phosphines [10] and phosphites [11].

The mass spectrum of $CpMn(CO)_2(C{=}CHPh)$ contains an interesting ion of the composition $C_8H_5Mn^+$ (m/e 156), formed by the elimination of the cyclopentadiene molecule from the ion $CpMn(C{=}CHPh)^+$, which probably has the structure of manganese phenylacetenide, $PhC{\equiv}CMn^+$. The formation of metal acetylenide ions is characteristic for Mn and Re cyclopentadienyl complexes; the mass spectra of $CpMn(CO)_3$ and $CpRe(CO)_3$, in particular, contain the ions C_2HM^+ (M is Mn or Re, Tables 9 and 10, respectively). Metal acetylenide ions

TABLE 9

MASS SPECTRUM OF $CpMn(CO)_3^+$ (T_i = 20°C)

Ion	m/e	Relative intensity	Ion	m/e	Relative intensity
P^+	204	25	C_2HMn^+	80	7
$P - CO^+$	176	7	$CHMn^+$	68	2
$P - 2CO^+$	148	26	$C_5H_6^+$	66	8
$P - 3CO^+$	120	100	$C_5H_5^+$	65	4
$C_3H_2Mn^+$	93	7	MnH^+	56	4
C_3HMn^+	92	2	Mn^+	55	89

TABLE 10

MASS SPECTRUM OF CpRe(CO)3 (T_i = 20°C)

Ion	*m/e*	Relative intensity	Ion	*m/e*	Relative intensity
P^+	336	50	$C_3H_2Re^+$	225	17
$P-CO^+$	308	24	C_3HRe^+	224	26
$P-2CO^+$	280	100	C_2HRe^+	212	4
$P-3CO^+$	252	58	$CHRe^+$	200	18
$C_5H_3Re^+$	250	27	CRe^+	199	5
C_5HRe^+	248	5	Re^+	187	5
$C_3H_3Re^+$	226	20			

possess high stabilities and may formally be regarded as structures containing stable doubly charged metal cations and acetylenide anions, $HC{\equiv}C^-M^{++}$ [12].

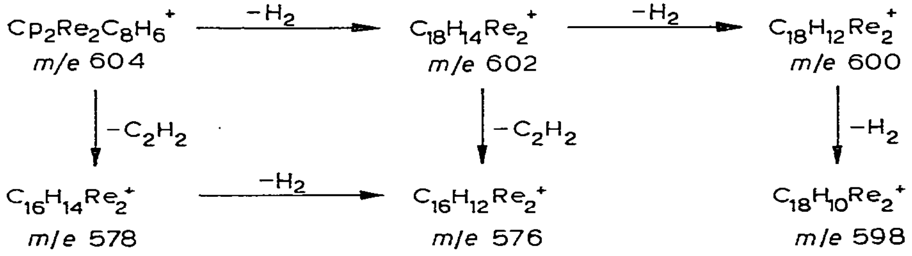
The mass spectrum becomes much more complex on the replacement of Mn in I with Re, that is on going to $CpRe(CO)_2(C{=}CHPh)$ (II). Thus a dramatic increase in intensity of decarbonylation ions is observed; two additional fragmentation processes occur that are absent from the mass spectrum of the manganese complex. These are the fragmentation of the cyclopentadienyl ring leading to the ions C_nH_nRe (n = 1,3) and a very intense dehydrogenation process. Similar phenomena are observed on going from $CpMn(CO)_3$ to $CpRe(CO)_3$.

The mass spectra of the binuclear Mn and Re complexes (V and VI) differ significantly from each other, first of all in that the mass spectrum of V contains intense ions $CpMn(CO)_3^+$ and their fragmentation products, probably resulting from thermal decomposition of the complex in the ion source. Apart from that, the mass spectra differ in binuclear ion intensities. The sum of the intensity of binuclear ions only amounts to 1% of the total ion current in the spectrum of the Mn complex, whereas the rhenium derivative fragments to give 70% of binuclear ions. It thus appears that the Mn—Mn bond is less stable than the Re—Re.

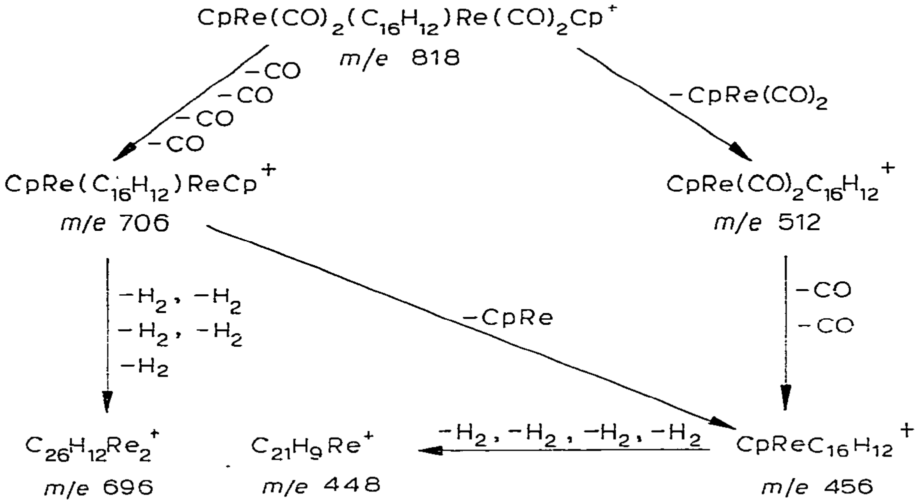
The molecular ion VI consecutively loses four carbonyl groups to give the base ion $Cp_2Re_2C_8H_6^+$ which further fragments by the usual scheme for rhenium cyclopentadienyl complexes, via the elimination of the H_2 and C_2H_2 neutral molecules [2,4] (see Scheme 2).

The ($P-4$ CO)$^+$ ion in the mass spectrum of 2,3-diphenylbutadienylidene complex (VIII) consecutively loses five(!) hydrogen molecules to give the ion

Scheme 2. Fragmentation of the ion $Cp_2Re_2C_8H_6^+$



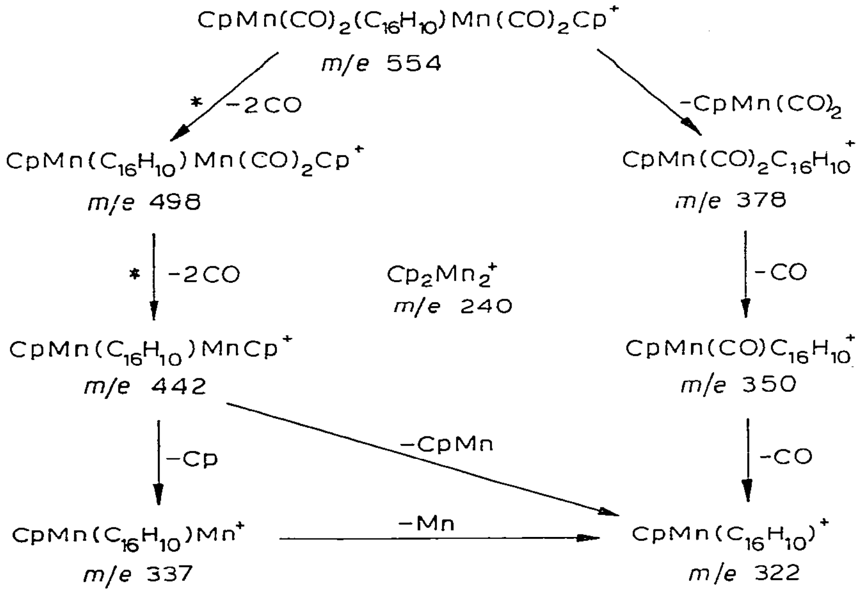
Scheme 3. Fragmentation of the molecular ion VIII.



$C_{26}H_{12}Re_2^+$ (*m/e* 696, Scheme 3). This seems to be the first example of such a large dehydrogenation under electron impact.

Undoubtedly, the rhenium atom plays the most important part in this process of successive elimination of five hydrogen molecules, unparalleled in organic mass spectrometry. "Internal catalysis" by the central rhenium atom is probably the moving force of the process. It should be noted that no such processes are observed with manganese complexes.

Scheme 4. Fragmentation of the molecular ion VII



The catalytic properties of rhenium and manganese are known to differ drastically [13]. The processes involving molecular oxygen are characteristic of manganese catalysis whereas rhenium is an efficient catalyst of hydrogenation-dehydrogenation reactions.

Dehydrogenation probably occurs via hydrogen transfer to the metal atom. Therefore the process should depend mainly on coordinative undersaturation of the ion involved. In fact, no dehydrogenation is observed until after the elimination of one or several ligands from the molecular ion.

Comparison of fragmentations of the $CpRe^+$ ion in the mass spectrum of $CpRe(CO)_3$ and of the ions $CpRe(C_{16}H_{12})ReCp^+$ and $CpReC_{16}H_{12}{}^+$ in the mass spectrum of VIII provides information about the source of hydrogen atoms. The elimination of hydrogen is likely to occur from both cyclopentadienyl and vinylidene ligands (CpRe successively loses two hydrogen molecules, $CpReC_{16}H_{12}{}^+$ loses four and $CpRe(C_{16}H_{12})ReCp$ five molecules). Unlike most transition metal mono- and bi-nuclear cyclopentadienylcarbonyl complexes which fragment exclusively by successive elimination of carbonyl ligands, the P^+ ions from VII and VIII also eliminate the $CpM(CO)_2$ particle (M = Mn, Re) (see Schemes 3 and 4) to give $CpMn(CO)_2(C_{16}H_{10})^+$ (*m/e* 378) and $CpRe(CO)_2(C_{16}H_{12})^+$ (*m/e* 512). This observation supports the suggestion that no metal—metal bonds occur in the complexes.

Experimental

The mass spectra of I, III—V, VII, IX, X were recorded on an MX-1303 instrument and those of II, VI, and VIII on an AEI MS-30 spectrometer equipped with a DS-50 data processing system. The conditions were: ion source temperature 150° C, direct inlet system temperature 40—190° C. Inlet system temperatures (T_i) are indicated in Tables 1 to 10 for each particular compound.

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