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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XIX *. CYMANTRENE-CYCLOPENTADIENYLMETAL CARBONYL DERIVATIVES

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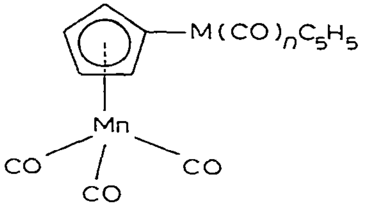
Summary

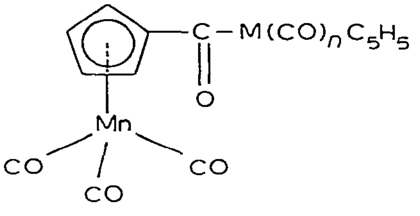
Mass spectra of the complexes π-$C_5H_5M(CO)_nXC_5H_4Mn(CO)_3$ have been studied. The presence of intense ions $C_5H_5M(CO)_nMn^+$ suggests that synthesis of new compounds with charged bivalent manganese of π-$C_5H_5W(CO)_3Mn^+X^-$ type is possible. In addition, the presence of these ions indicates preferential loss of the first three carbonyl groups from the manganese atom.

Earlier, we studied the mass spectra of some bimetallic derivatives of cyclopentadienylrhenium tricarbonyl and cyclopentadienylmanganese tricarbonyl containing vinylidene ligands [2].

The purpose of this work is the study of mass spectra of derivatives of cyclopentadienylmanganese tricarbonyl in which one of the hydrogen atoms is substituted by a π-cyclopentadienylmetal carbonyl radical (Ia—c to IVa—c, in all cases a, M = Fe, n = 2; b, M = Mo, n = 3; c, M = W, n = 3).



(Ia—c)



(IIa—c)

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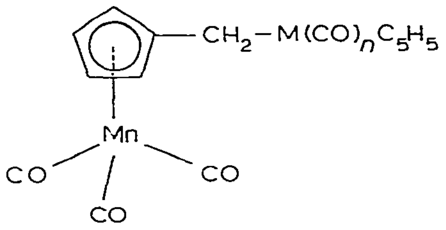
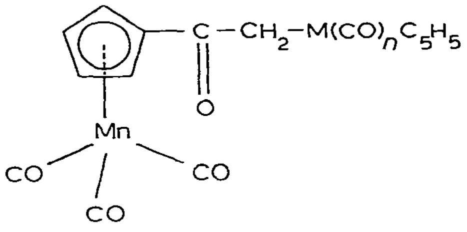
[*] For Part XVIII see ref. 1.



(IIIa−c)



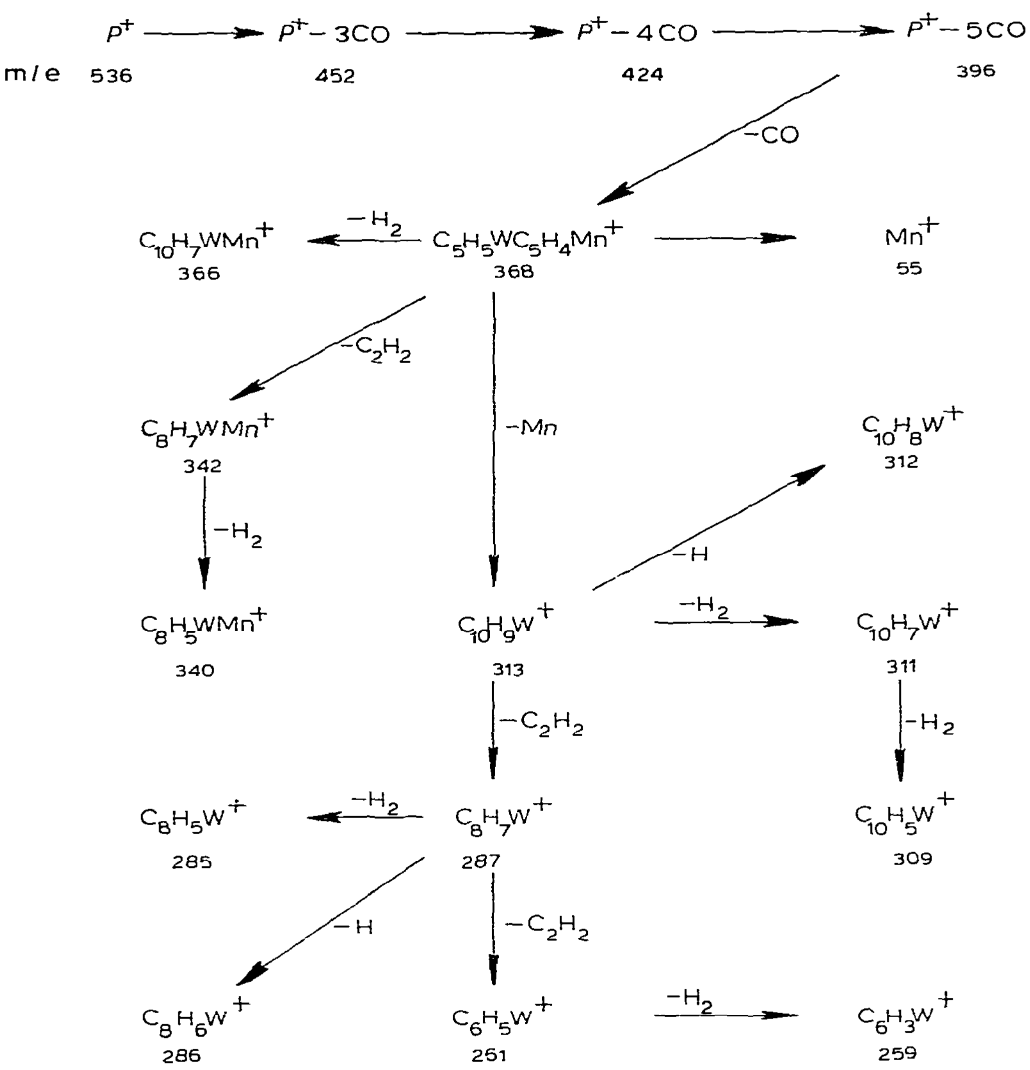
(IVa−c)

The only path of fragmentation for molecular ions of complexes Ia—c is a successive decarbonylation up to the formation of ions $C_5H_5MC_5H_4Mn^+$, which are the base peak in the mass spectra of these compounds (Table 1, Scheme 1). Their further degradation with successive loss of a manganese atom and two acetylene molecules in the case of the tungsten complex Ic is followed by the elimination of a hydrogen molecule. $C_{10}H_9M^+$ (M = Mo, W) ions also undergo dehydrogenation, which probably takes place with the participation of a metal

TABLE 1

MASS SPECTRA OF $C_5H_5M(CO)_nC_5H_4Mn(CO)_3$(1a—C)

Ion	Relative intensity (%)		
	M = Fe	Mo	W
P^+	15	2	49
$P^+ - CO$	1	9	—
$P^+ - 2\,CO$	9	0.4	—
$P^+ - 3\,CO$	19	24	57
$P^+ - 4\,CO$	10	15	39
$P^+ - 5\,CO$	100	25	82
$P^+ - 6\,CO$	—	100	100
$P^+ - nCO - H_2$	—	—	5
$P^+ - nCO - C_2H_2$	1	1	4
$P^+ - nCO - C_2H_2 - H_2$	—	—	2
$P^+ - nCO - Mn$	11	22	57
$P^+ - nCO - C_5H_5$	3	—	—
$P^+ - nCO - Mn - H_2$	—	21	12
$C_{10}H_9M^+$	4	6	7
$C_8H_7M^+$	7	14	30
$C_8H_6N^+$	—	7	7
$C_8H_5M^+$	—	6	14
$P^+ - nCO - 2H_2$	—	—	3
$C_6H_5M^+$	2	6	3
$C_6H_3M^+$	—	—	5
$C_5H_5M^+$	10	—	—
$C_3H_3M^+$	1	2	—
$C_3H_2M^+$	—	—	2
C_3HM^+	—	—	2
$C_5H_3M^+$	—	4	—
$C_{10}H_9^+$	32	—	—
$C_8H_7^+$	2	—	—
C_2HM^+	4	—	—
$C_5H_5Mn^+$	2	—	—
M^+	18	3	—
Mn^+	20	12	41



SCHEME 1
Fragmentation of $C_5H_5W(CO)_3C_5H_4Mn(CO)_3$ (Ib)

atom according to the mechanism of "internal catalysis" we described earlier for complexes of rhenium [2].

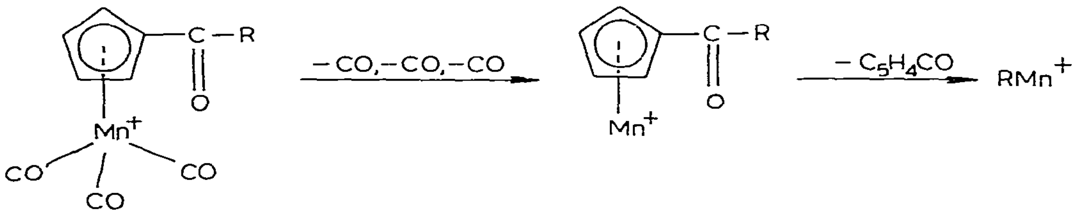
The acyl derivatives of cymantrene, $(CO)_3MnC_5H_4COM(CO)_nC_5H_5$ (IIa—c), do not form molecular ion peaks (Table 2). The heaviest ion in their mass spectra are $P^+ - CO$ ions. Their fragmentation is practically identical to the breakdown of complexes Ia—c and the spectra of molybdenum derivatives Ib and IIb coincide fully. The only characteristic fragmentation pathway of acyl complexes IIa, IIc is loss of the neutral molecule C_5H_4CO from the $P^+ - 3$ CO ion, which is followed by the migration of the $C_5H_5M(CO)_n$ radical to the manganese atom with the formation of the $C_5H_5M(CO)_nMn^+$ ion which has the maximum intensity in the mass spectrum of the tungsten complex (Table 2, Scheme 2). This process is analogous to the well-known rearrangement taking

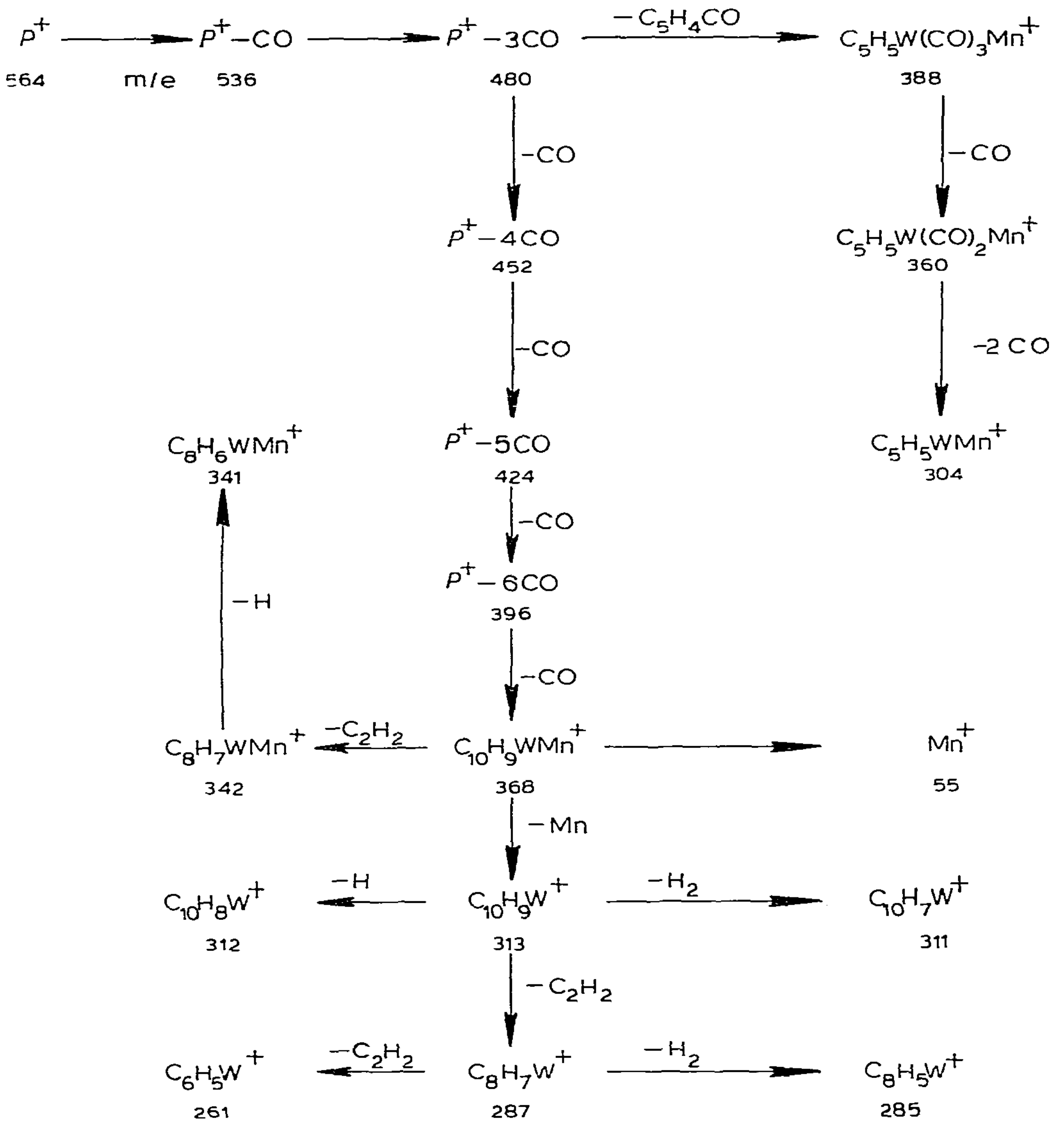
TABLE 2

MASS SPECTRA OF $C_5H_5M(CO)_nCOC_5H_4Mn(CO)_3$ (IIa—c)

Ion	Relative intensity (%)		
	M = Fe	Mo	W
P^+	—	—	—
$P^+ - CO$	13	3	86
$P^+ - 2\ CO$	8	8	—
$P^+ - 3\ CO$	11	—	7
$P^+ - 4\ CO$	27	17	41
$P^+ - 5\ CO$	8	11	23
$P^+ - 6\ CO$		22	66
$C_5H_5MC_5H_4Mn^+$	100	100	78
$P^+ - nCO - C_2H_2^+$	—	—	3
$C_8H_6MMn^+$	—	—	4
$C_{10}H_9M^+$	10	23	60
$C_{10}H_8M^+$	—	7	6
$C_{10}H_7M^+$	—	23	6
$C_8H_7M^+$	5	17	21
$C_8H_6M^+$	—	6	2
$C_8H_5M^+$	—	7	12
$C_6H_5M^+$	2	11	4
$C_6H_3M^+$	—	—	1
$MnC_5H_4M^+$	3	—	—
$C_5H_5M^+$	21	—	11
$C_5H_4M^+$	—	4	—
$C_5H_3M^+$	—	—	4
$C_3H_3M^+$	3	—	—
$C_3H_2M^+$	6	—	—
C_3HM^+	—	—	2
C_3M^+	—	—	3
CH_2M^+	—	—	8
CHM^+	—	—	6
$C_{10}H_9^+$	28	—	—
$C_8H_7^+$	2	—	—
$C_5H_5M(CO)_nMn^+$	15	—	100
$C_5H_5M(CO)_{n-1}Mn^+$	5	—	20
$C_5H_5M(CO)_{n-2}Mn^+$	3	—	—
$C_5H_5MMn^+$	—	—	4
MMn^+	3	—	—
M^+	15	2	—
$C_5H_5Mn^+$	—	4	5
$C_5H_4Mn(CO)_2^+$	—	—	3
$C_5H_4Mn(CO)^+$	—	—	4
$C_5H_4Mn^+$	—	—	6

place in acylcymantrenes under electron impact with the migration of the substituent to the manganese atom according to the scheme:





SCHEME 2
Fragmentation of $C_5H_5W(CO)_3COC_5H_4Mn(CO)_3$ (IIb)

The driving force for this rearrangement is the localization of the positive charge on the manganese atom to which the group R migrates. Taking this into consideration one may suppose that in the molybdenum complex where this rearrangement is not characteristic, the charge is localized on the molybdenum atom. This is in accordance with the lower ionization potential of molybdenum (7.10 eV) in comparison with the ionization potential of manganese (7.43 eV), iron (7.89 eV) and tungsten (7.98 eV) [3].

$C_5H_5W(CO)_3Mn^+$ and $C_5H_5Fe(CO)_2Mn^+$ ions are isoelectronic with the corresponding complex of cyclopentadienylmetal halide namely, $C_5H_5W(CO)_3Cl$ and $C_5H_5Fe(CO_2)Cl$, and probably have similar structure. The high intensity of

TABLE 3

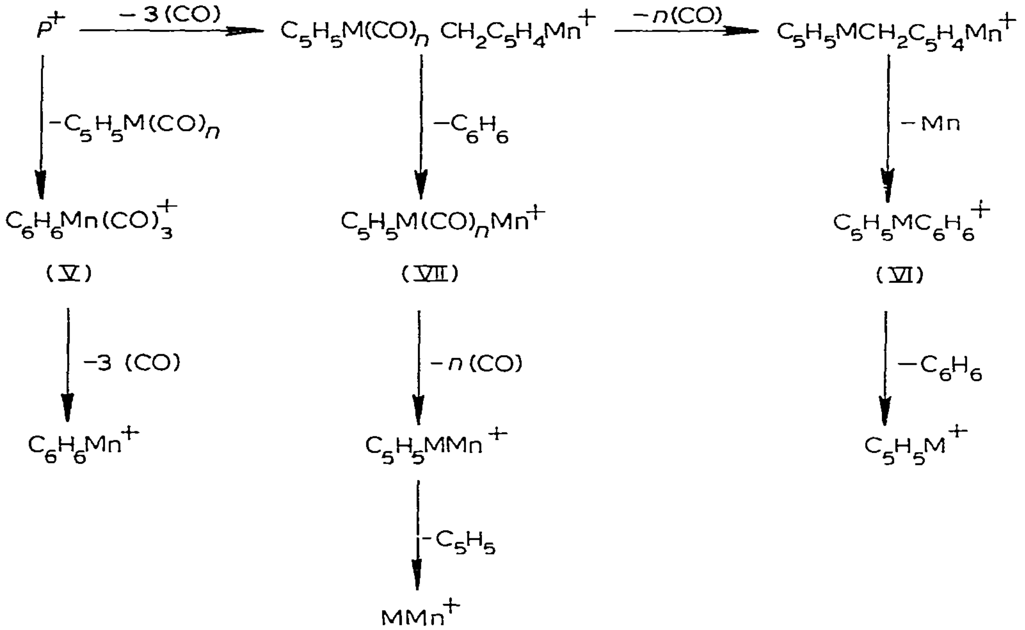
MASS SPECTRA OF $C_5H_5M(CO)_nCH_2C_5H_4Mn(CO)_3$ (IIIa—c)

Ion	Relative intensity (%)		
	M = Fe	Mo	W
P^+	0.8	—	3
$P^+ - CO$	0.2	4	0.7
$P^+ - 2\,CO$	0.3	—	—
$P^+ - 3\,CO$	2	2	3
$P^+ - 4\,CO$	3	5	4
$P^+ - 5\,CO$	17	7	3
$P^+ - 6\,CO$		18	8
$C_5H_5M(CO)_3Mn^+$		39	61
$C_5H_5M(CO)_2Mn^+$	42	19	26
$C_5H_5M(CO)Mn^+$	5	—	10
$C_5H_5MMn^+$	5	9	7
MnM^+	5	—	—
$C_6H_6Mn(CO)_3^+$	74	100	89
$C_6H_6Mn(CO)_2^+$	7	13	11
$C_6H_6Mn(CO)^+$	26	44	27
$C_6H_6Mn^+$	16	36	18
$C_6H_6^+$	7	12	17
$C_5H_5M(CO)_2^+$	3	6	—
$C_5H_5M(CO)^+$	4	—	7
$C_5H_5M^+$	88	55	7
$C_3H_3M^+$	4	—	5
$C_3H_2M^+$	—	—	3
C_3HM^+	—	—	3
C_2HM^+	3	—	—
M^+	14	9	—
$C_5H_5Mn^+$	—	9	—
Mn^+	20	100	100
$C_9H_8MMn^+$	—	13	10
$C_5H_5MC_6H_6^+$	100	91	32
$C_{11}H_9M^+$	—	29	23
$C_9H_7M^+$	—	36	20
$C_7H_7M^+$	—	27	—
$C_3H_3M(CO)^+$	—	13	—

these ions (in the mass spectrum of the tungsten complex it is maximum) proves their high stability.

Some examples are known where the formation of certain ions was first observed in the gas phase under the conditions of mass spectrometry and they were later synthesized in the condensed phase. This refers for instance, to the three-layer sandwiches [4] or ions $C_5(CH_3)_5Sn^+$ [5]. Therefore, there is a possibility of the synthesis of new compounds with a charged two-valent manganese atom of π-$C_5H_5W(CO)Mn^+\ X^-$ type.

Unlike the acyl complexes during the fragmentation of methylene derivatives of cymantrene $C_5H_5M(CO)_nCH_2C_5H_4Mn(CO_3)$ (IIIa—c), the ions $C_5H_5M(CO)_n$-Mn^+ are formed with all metals (Table 3). This is probably connected with the stabilizing influence of the methylene group which form together with the cyclopentadienyl ring a 6-electron benzene ligand and stabilizes the coordinatively unsaturated manganese atom more effectively in comparison with the C_5H_4CO group (Scheme 3). The presence of $C_5H_5M(CO)_nMn^+$ ions in the spec-



SCHEME 3
Fragmentation of $C_5H_5M(CO)_nCH_2C_5H_4Mn(CO)_3$ (IIIa—c)

tra of IIa, IIc and IIIa—c enables us to determine the mechanism of decarbonylation of molecular ions of these compounds. While it is impossible to find the order of decarbonylation for Ia—c without an isotope label, the presence of $C_5H_5M(CO)_nMn^+$ ions in mass spectra of IIa, IIc and IIIa—c proves the preferential loss of the first three carbonyl groups from the manganese atom.

Another way of fragmentation of molecular ions of methylene complexes $C_5H_5M(CO)_nCH_2C_5H_4Mn(CO)_3$ (IIIa—c) is the process of rupture of the metal—CH_2 bond (the process follows decarbonylation) with the formation of intense $C_6H_6Mn(CO)_3^+$ ions which probably have the structure of an eighteen electron cation of π-benzenemanganese tricarbonyl (Scheme 3). It should be noted that the synthesis of such complexes in the condensed phase has already been carried out [6].

In methylene complexes IIIa—c the process of complete decarbonylation with the further removal of a manganese atom also takes place. This process is characteristic for the whole series of the compounds studied. The $C_5H_5MC_6H_6^+$ ions formed in this process are of high intensity and probably have the structure of the corresponding benzenecyclopentadienyl complex. It should be noted that the ionic complexes of π-benzenecyclopentadienyliron $[C_6H_6FeC_5H_5]^+X^-$ are also synthesized under normal experimental conditions [7].

So, during the fragmentation of methylene derivatives of cymantrene (IIIa —c) three interesting types of ions, namely benzenemanganese tricarbonyl (V), benzenecyclopentadienylmetal (VI) and cyclopentadienylmetaltri(di)carbonylmanganese (VII), are formed. The first two types of V and VI cations are obtained under normal experimental conditions as salts. This proves once more the conclusion about the possibility of synthesis of type VII ionic complexes.

Complexes IVa—c containing the —$COCH_2$— group have a very low thermal stability. The ions formed during the ionization of thermolysis products of these molecules are the most intense in the mass spectra. These products are bicymantrene, acetylcymantrene and ferrocene. The IVa—c molecular ions fragmentation pattern is similar to that of Ia—c. This fragmentation consists of a successive decarbonylation with the further removal of a manganese atom.

Experimental

The mass spectra were recorded using an AEI MS-30 apparatus with a DS-50 data system under in the following conditions: temperature of the direct inlet system 20—200° C, temperature of the source 200° C, ionizing voltage 70 V, emission current 100 mA. Monoisotopic spectra were computed according to the AELITA program [8]. The syntheses of I—IV were carried out using previously published methods [9—13].

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