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MASS SPECTRA OF π-BONDED ORGANOMETALLIC COMPOUNDS. (1)

N. Maoz, Asher Mandelbaum and Michael Cais
Department of Chemistry, Technion - Israel Institute of Technology
Haifa, Israel.

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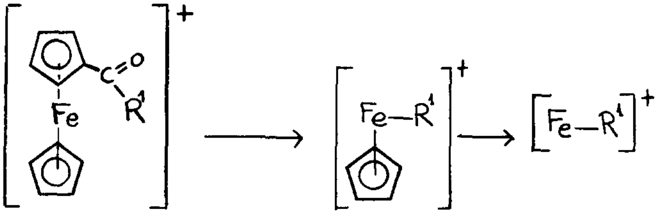
In a recent communication (2) we reported some preliminary results on the fragmentation of ferrocenes containing a carbonyl substituent in the α-position to the cyclopentadienyl ring.

One of the more interesting observations reported for these compounds was the appearance of fragments II in the mass spectra of ferrocene derivatives of structure I. These fragments, II, arising from the transfer of the group R^1 to the metal atom with concomitant cleavage of the bond between the substituted cyclopentadienyl ring and the iron atom, then gave rise to the ions III by cleavage of the remaining cyclopentadienyl ring.

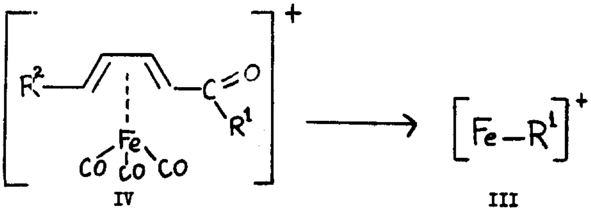


I II III

We now wish to report further results obtained in our laboratory in the course of a systematic investigation of mass spectral measurements of π-bonded organometallic compounds.

The same type of fragmentation pattern, leading to formation of ions such as III, appears to be a much more general phenomenon than might have been anticipated just on the basis of our ferrocene results (2).

Thus, an analysis of the fragmentation pattern of substituted butadieneiron tricarbonyls, IV, under electron impact (3), showed the presence of fragment III in all the spectra we have investigated so far.

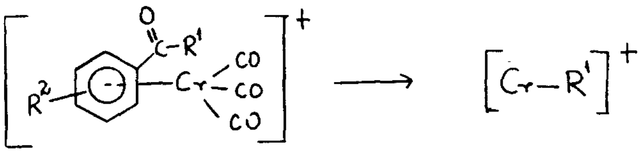


The m/e values and the abundance (% Σ_{50}) of the major fragments observed in the mass spectra of IV are tabulated in Table 1.

The same type of fragmentation was observed in the mass spectra of substituted arenechromium tricarbonyl derivatives, V, and substituted cymantrenes, VII, (4).

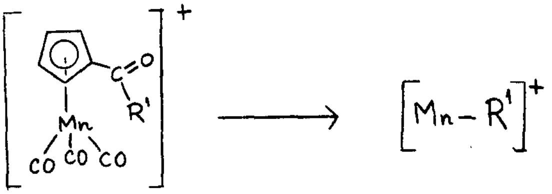
The data for the major fragments observed in the mass spectra of several of the compounds V and VII are given in Tables 2 and 3 respectively.

It is interesting to note at this point that the ion $[\text{Metal-R}^1]^+$ has even been observed in the mass spectra of compounds where R^1 is not immediately attached to the carbon atom in the α-position to the π-hydrocarbonmetal system. (See for example compounds 3b and 3c in Table 3). The



V

VI



VII

VIII

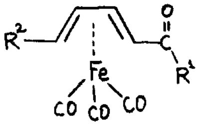
effect of the position of substituents in the fragmentation pattern of π-bonded organometallic compounds is being further investigated in our laboratory.

A rather surprising result observed in the mass spectra of the π-hydrocarbonmetal tricarbonyl derivatives investigated is the appearance of a fragment whose m/e value corresponds to $[LR^1M]^+$, (where L=hydrocarbon ligand and M= metal atom). This arises from the molecular ion $[(L-\overset{O}{C}-R^1)M(CO)_3]^+$ minus the three carbon monoxide carbonyls giving $[(L-\overset{O}{C}-R^1)M]^+$, followed by the loss of the carbonyl function to which the R^1 substituent is attached.

The suggested pattern of fragmentation, namely $[(L-\overset{O}{C}-R^1)M(CO)_3]^+ \longrightarrow$ $\longrightarrow [LR^1M]^+$ is supported by the observation of the corresponding metastable peaks (in several of the measured spectra) as well as by finding the expected isotopic abundance (in the case of the iron and chromium derivatives).

TABLE 1

m/e Values (and Abundance % Σ_{50}) of Major Fragments in the Mass Spectra of Dieneiron Tricarbonyls



ION$^+$	Compound 1a	 1b	 1c	 1d	 1e	 1f
L.Fe(CO)$_3$	252 (3.43)	253	251 (1.63)	253	282 (2.37)	310 (1.31)
L.Fe(CO)$_2$	224 (3.6)	225	223 (4.9)	225	254 (3.34)	282 (1.09)
L.Fe(CO)	196 (6.27)	197	195 (9.18)	197	226 (6.56)	254 (2.56)
L.Fe	168 (14.1)	169	167 (13.3)	169	198 (3.23)	226 (3.33)
L	112 (1.25)	113	111 (1.48)	113	142 (0.64)	170 (0.65)
Fe-R^1	73 (2.82)	74	72 (2.07)	74	73 (4.5)	87 (4.1)
Fe	56 (8.95)	56	56 (5.76)	56	56 (4.63)	56 (5.85)

	a	b	c	d	e	f
R^1 =	OH	CD	NH_2	ND_2	OH	OCH_3
R^2 =	CH_3	CH_3	CH_3	CH_3	CO_2H	CO_2CH_3

L = Diene Ligand

TABLE 2

m/e Values (and Abundance % Σ_{50}) of Major Fragments
in the Mass Spectra of Arenechromium Tricarbonyls
ArHCr(CO)$_3$

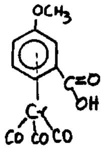
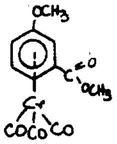
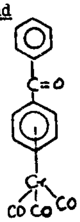
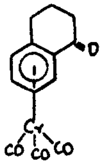
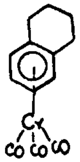
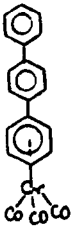
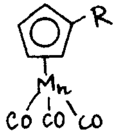
	Compound					
ION$^+$	 2a	 2b	 2c	 2d	 2e	 2f
ArHCr(CO)$_3$	288 (5.2)	302 (5.3)	318 (2.65)	282 (5.0)	268 (3.86)	366 (3.35)
ArHCr(CO)$_2$	-	-	290 (0.82)	-	-	-
ArHCr(CO)	232 (1.6)	246 (2.12)	262 (4.9)	226 (3.0)	212 (1.7)	310 (5.2)
ArHCr	204 (18.2)	218 (24.7)	234 (25.5)	198 (24.0)	184 (18.0)	282 (20.2)
ArH	152 (2.46)	166 (0.7)	182 (0.61)	146 (0.5)	132 (3.3)	230 (12.7)
Cr-R^1 (R^1= OH)	69 (2.02)	-	-	-	-	-
Cr-R^1 (R^1=OCH$_3$)	-	83 (0.7)	-	-	-	-
Cr	52 (20.2)	52 (25.9)	52 (30.2)	52 (30.0)	52 (32.6)	52 (20.7)

TABLE 3

m/e Values (and Abundance % Σ_{50}) of Major Fragments in the Mass Spectra of Cymantrenes

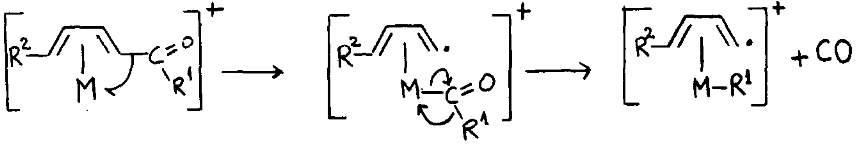


ION$^+$	Compound R: $-\overset{O}{\overset{\|}{C}}-OH$ 3a	$-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ 3b	$-CH=CH-\overset{O}{\overset{\|}{C}}-OH$ 3c
$L.Mn(CO)_3$	248(7.5)	276(0.76)	274(5.95)
$L.Mn(CO)_2$	220(0.13)	248(1.51)	246(0.32)
L.Mn(CO)	192(4.85)	220(1.51)	218(4.34)
L.Mn	164(34.1)	192(10.6)	190(15.7)
Mn-OH	72(17.7)	72(9.5)	72(6.44)
Mn	55(12.4)	55(8.34)	55(13.8)

$L = C_5H_4$

The possible generality of this type of fragmentation is hinted at by the variety of examples enumerated in Table 4.

We should like to note that as far as we are aware there are no reported examples of similar decarbonylation of carboxylic acids, or their derivatives, under electron impact. Indeed, our own measurements of metal-free diene carboxylic acids do not show such decarbonylations. Moreover, we have observed that the peak corresponding to such decarbonylation is also absent from the mass spectra of π-organometallic compounds in which the group $-\overset{O}{\overset{\|}{C}}-R^1$ is not directly bonded to the metal-carrying π-organic moiety (for example compounds such as 3b and 3c in Table 3). This observation has led us to suggest a possible mechanism of decarbonylation under electron impact in which the second step, migration of R^1 from $\overset{O}{\overset{\|}{C}}-R^1$ to the metal might be considered analogous to the methyl migration recently suggested (5) in the mechanism for the thermal decarbonylation of acetylmanganese pentacarbonyl, $CH_3COMn(CO)_5$.



The next feature of interest we wish to mention in this preliminary communication, has been observed in the mass spectra of π-bonded organometallics containing two or more metal atoms per molecule.

The data for some of the compounds investigated are summarized in Tables 5 and 6 and the structural formulae of these compounds are drawn in Fig.1.

TABLE 4

m/e Values, Abundances (% Σ_{50}) and Metastable Peaks of Fragments Involved in Exhaustive Decarbonylation.

$$\left[(L-\overset{O}{\overset{\|}{C}}-R^1)M(CO)_3\right]^+ \longrightarrow \left[(L-\overset{O}{\overset{\|}{C}}-R^1)M\right]^+ \longrightarrow \left[LR^1M\right]^+$$

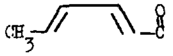
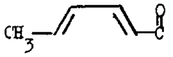
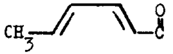
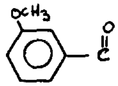
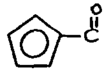
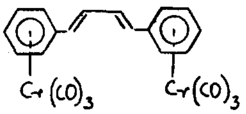
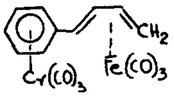
Compound No.	$L-\overset{O}{\overset{\|}{C}}$	R^1	M	m/e of $[LR^1M]^+$	$\%\Sigma_{50}$	metastable peak m/e
1a		OH	Fe	140	8.65	116.5
1b		OD	Fe	141	6.0	
1c		NH_2	Fe	139	3.55	115.8
1d		ND_2	Fe	141	2.3	
1e		OH	Fe	170	1.18	146
1f		OCH_3	Fe	198	2.33	173.5
2a		OH	Cr	176	3.04	152
3a		OH	Mn	136	0.71	

Fig 1

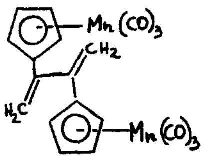
Structural Formulae of Compounds Collected in Tables 5 and 6.



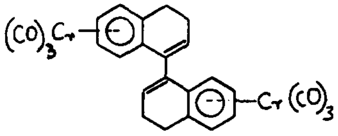
5a



5 f



6 a



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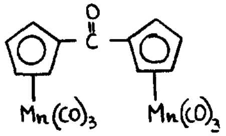

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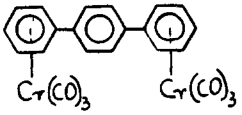
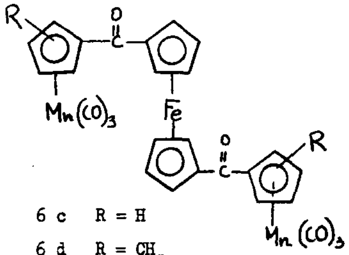
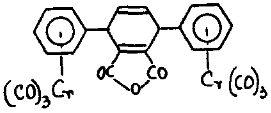


5 c

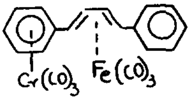


6 c R = H

6 d R = CH_3



5 d



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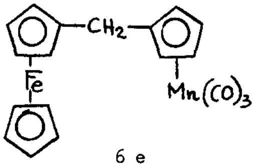

6 e

TABLE 5

m/e Values (and Abundance % Σ_{50}) of Major Fragments in the Mass Spectra of π-Bonded Organometallics Containing Two Chromium or Chromium and Iron Atoms in the same Molecule.

ION$^+$	5a	5b	5c	5d	5e	5f
$LM^1M^2(CO)_6$	478(0.25)	530(1.35)	502(0.97)	574(0.1)	482(3.78)	406(4.85)
$LM^1M^2(CO)_5$	-	-	-	546(0.2)	-	-
$LM^1M^2(CO)_4$	-	-	-	518(0.2)	426(0.87)	350(3.0)
$LM^1M^2(CO)_3$	394(0.25)	446(1.46)	418(1.52)	490(0.61)	398(3.88)	322(6.89)
$LM^1M^2(CO)_2$	-	418(2.25)	390(1.1)	462(0.2)	370(3.97)	294(5.15)
$LM^1M^2(CO)$	-	-	362(1.65)	-	342(2.81)	266(8.8)
LCrCr	-	362(3.7)	334(1.52)	406(0.92)	-	-
LCrFe	-	-	-	-	314(12.9)	238(8.8)
LFe	-	-	-	-	262(1.26)	186(2.9)
LCr	258(15.0)	310(8.2)	282(14.5)	354(13.7)	258(8.25)	182(6.65)
L	206(8.55)	258(4.85)	230(9.4)	302(4.3)	206(1.26)	130(0.32)
Cr-Fe	-	-	-	-	108(1.45)	108(3.32)
Cr-Cr	104(0.38)	104(0.1)	104(0.28)	-	-	-
Fe	-	-	-	-	56(2.13)	56(1.83)
Cr	52(14.0)	52(9.0)	52(17.6)	52(15.8)	52(12.7)	52(13.5)

L = Hydrocarbon Ligand (see Fig.1)

TABLE 6

m/e Values (and Abundance % Σ_{50}) of Major Fragments in the Mass Spectra of π-Bonded Organometallics Containing Two Manganese or Manganese and Iron Atoms in the same Molecule.

ION$^+$	6a	6b	6c	6d	6e
$LM^1M^2(CO)_6$	458(12.8)	434(6.35)	646(7.5)	674(8.8)	-
$LM^1M^2(CO)_3$	374(7.05)	350(10.8)	562(4.4)	590(3.13)	402(12.9)
$LM^1M^2(CO)_2$	346(0.38)	322(0.53)	-	-	-
$LM^1M^2(CO)$	318(9.15)	294(8.8)	-	-	-
LMnMn	290(15.0)	266(18.3)	478(24.1)	506(23.2)	-
LMnFe	-	-	-	-	318(21.3)
LFe	-	-	-	-	263(1.33)
LMn	235(17.1)	211(3.18)	-	451(<0.1)	-
L	180(1.9)	156(0.53)	368(1.07)	396(<0.1)	-
Mn-Fe	-	-	111(<0.1)	111(<0.1)	111(0.33)
Mn-Mn	110(0.57)	110(1.23)	-	-	-
Fe	-	-	56(1.29)	56(0.63)	56(2.0)
Mn	55(9.5)	55(15.6)	55(3.52)	55(1.57)	55(2.83)

L = Hydrocarbon Ligand (see Fig.1)

These compounds under electron impact give rise to ions whose m/e values correspond to the $[M^1 - M^2]^+$ ion. We have observed the following ions: $[Cr - Cr]^+$, $[Cr - Fe]^+$, $[Fe - Mn]^+$ and $[Mn - Mn]^+$. In the case of the ions containing the iron and chromium atoms, the $[M^1 - M^2]^+$ ion has been confirmed by isotopic abundance measurements.

Another interesting feature observed for polymetal complexes has to do with the way carbon monoxide is lost from the metal tricarbonyl moieties.

In the case of dieneiron tricarbonyl compounds (Table 1) the carbon monoxide groups are lost in a stepwise manner. The same is true for cymantrene derivatives (Table 3) and for some of the arenechromium tricarbonyl compounds (Table 2).

The same cracking pattern, namely stepwise loss of carbon monoxide groups, one at a time, has also been reported for the hexacarbonyls of chromium, molybdenum and tungsten (6).

However, this pattern of fragmentation is completely altered the moment there are at least two metal atoms in the same molecule bonded in <u>suitable positions</u>.

For instance the dichromium derivative 5b (Table 5) shows the ions corresponding to the loss of three, four and six carbon monoxide groups with no intermediate steps whereas the dichromium derivative 5a (Table 5) does exhibit the stepwise loss of carbon monoxide.

This feature is most strikingly shown by the data for the manganese tricarbonyl derivatives collected in Table 6. In all these compounds, which contain either two manganese atoms, or one manganese and one iron atoms, or two manganese and one iron atoms, three carbon monoxide groups are lost in one step. Moreover, in the case of compounds 6c and 6d even the remaining three carbon monoxide groups are lost in one step. This suggested pattern is supported by the presence of the required metastable peaks in all the measured spectra.

We cannot yet offer a suitable explanation for this phenomenon. We might mention, in this connection, a recent report of a concerted elimination of two radicals which are initially attached to the same metal atom and which is ascribed to changes of valency of the bonded metal atom occuring during the ion dissociation reactions (7).

A final point which should be mentioned in this communication is the advantageous use we have made of the mass spectra of ferrocenes for distinguishing between homo- and hetero- disubstituted ferrocenes. The presence or absence of the peak m/e = 121 for the ion $\left[C_5H_5Fe\right]^+$ in the mass spectra of ferrocenes (2) may turn out to be a more sensitive criterion than the "9-10 μ rule" generally used in ferrocene chemistry (8).

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1. a) Organometallic Studies. Part XIV; Part XIII, M. Cais and A. Eisenstadt Revue Roumaine de Chimie, in press.

   b) Studies in Mass Spectrometry. Part III; Part II, H. Audier, M. Fétizon, D. Ginsburg, A. Mandelbaum and Th. Rüll, Tetrahedron Letters, 1, 13 (1965).

   c) This work has been sponsored in part by a P.L.480 Research Grant, U.S.D.A. Project UR-A10-(40)-34 and in part by the Air Force Materials Laboratory, Research and Technology Division, AFSC, through the European Office of Aerospace Research, United States Air Force, Contract No. AF 61(052)-752.

2. A. Mandelbaum and M. Cais, *Tetrahedron Letters*, *51*, 3847 (1964)

3. All the spectra were recorded on a type Atlas CH 4 mass spectrometer equipped with a direct inlet system. Ionisation energy was maintained at 70 ev and the ionisation current at 20 µA.

4. The name **CYMANTRENE** for *CY*clopentadienyl*MAN*ganese*TR*icarbonyl, $C_5H_5Mn(CO)_3$ analogous to **FERROCENE**, was suggested by M. Cais in a lecture at the XIXth International Congress of Pure and Applied Chemistry, London, July 10-17, 1963.

   On this basis, the radical $(CO)_3MnC_5H_4$ - is called cymantrenyl; $(CO)_3MnC_5H_4.CH_2$ - is *cymantryl*; and $(CO)_3MnC_5H_4.CH$ - is *cymantrylidene*. (Compare with the nomenclature suggested by J. Boichard, J.F. Monin and J. Tirouflet, *Bull. Soc. Chim. France*, 851 (1963) for analogous ferrocene derivatives.)

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6. R.E. Winkers and R.W. Kiser, *Inorg. Chem.*, *4*, 157 (1965)

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