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MASS SPECTRA OF (CHLOROHEXAFLUOROCYCLOPENTENYL)-MANGANESE AND -RHENIUM PENTACARBONYLS

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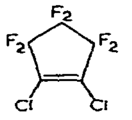
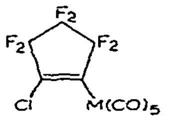
INTRODUCTION

In connection with work on chlorofluorocarbon complexes of some transition metals[1], we recently determined the mass spectra of the chlorofluorocarbon (I), and the derived complexes (II) and (III). Few mass spectra of transition metal–fluorocarbon complexes have been reported, those of $C_4F_8Fe(CO)_4$ and $C_6F_8Fe(CO)_4$ being described briefly[2]; we have previously[3] characterised the reaction product from hexafluoro-2-butyne and nickel carbonyl as $(C_4F_6)_3Ni_4(CO)_3$ from its mass spectrum and other data.



(I)



(II) M=Mn
(III) M=Re

DISCUSSION

Treatment of 1,2-dichlorohexafluorocyclopentene (I) with metal carbonyl anions affords the complexes (II) and (III), the manganese complex being characterised only on the basis of its infra-red and mass spectra[1]. The mass spectrum of (I) shows major peaks corresponding to the ions shown in Chart 1, which represents a plausible fragmentation scheme, since several processes are confirmed by the

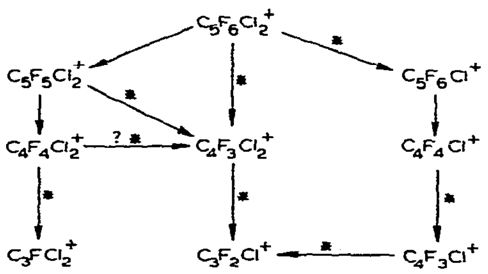


Chart 1. Fragmentation pathways for $C_5F_6Cl_2^+$. *Metastable peaks observed for these transitions (see Table 2).

necessary metastable transitions. The major process occurring after ionisation is loss of CF_3, followed by CFCl, to give the base peak $C_3F_2Cl^+$. Another contribution to the high abundance of this ion is probably successive loss of Cl, CF_2 and F to give $C_4F_3Cl^+$, which then loses CF. The parent ion may also lose F, CF and CF_3 to form $C_3FCl_2^+$.

Both complexes (II) and (III) showed similar fragmentation patterns, the first processes being the expected stepwise loss of CO groups to give $C_5F_6ClM(CO)_n^+$ ($n = 0$–5), and a ready loss of a fluorine atom giving $C_5F_5ClM(CO)_n^+$ ($n = 0$–5). Rupture of the metal–carbon σ-bond occurs to give both $C_5F_6Cl^+$ and $Mn(CO)_5^+$, presumably by the reactions:

$$C_5F_6ClM(CO)_5^+ \rightarrow C_5F_6Cl^+ + M(CO)_5 \qquad (1)$$

$$C_5F_6ClM(CO)_5^+ \rightarrow C_5F_6Cl + M(CO)_5^+ \qquad (2)$$

Only process (1) is characterised by a metastable transition (see Table 2) in the spectrum of complex (II), indicating this to be the preferred route, in agreement with the observed relative abundances [$C_5F_6Cl^+$, 24.5; $Mn(CO)_5^+$, 18%]. No metastable peaks are observed for either process for the rhenium complex; the relative abundances are reversed, and much lower (3 and 6%, respectively). Further fragmentation of $C_5F_6Cl^+$ seems to occur in a similar manner to that observed for the same ion formed from (I).

Comparison of the breakdown of $C_5F_6Cl_2^+$ with those of the ions $C_5F_6ClM^+$ (Charts 1 and 2) shows that the patterns are similar, the presence of two different atoms on the double bond resulting in two breakdown patterns, giving $C_3F_2M^+$ and $C_3F_2Cl^+$ as the end products. However, with the metal complexes, loss of CF_3 is a minor pathway, $C_4F_3ClMn^+$, for example, having a very small relative abundance, although loss of CFCl from this ion is confirmed by the appearance of the appropriate metastable peak. Comparison of the fragmentation patterns of (II) and (III) with that of (I) indicate similar processes to be operative in all cases; presence of the metal atom appears to facilitate simple loss of F or Cl, rather than CF_3. These observations may be rationalised by supposing that the initial electron may be lost from F

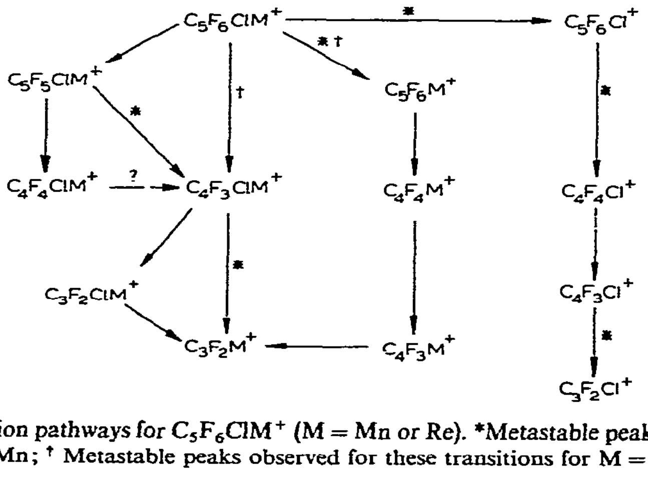


Chart 2. Fragmentation pathways for $C_5F_6ClM^+$ (M = Mn or Re). *Metastable peaks observed for these transitions for M = Mn; † Metastable peaks observed for these transitions for M = Re (see Table 2).

and Cl in (I), and also from the metal in (II) or (III); this results in an extra fragmentation pathway, as is shown in Chart 2.

Although peaks are observed corresponding to most combinations $C_mF_n^+$, corresponding to further fragmentation of $C_3F_2M^+$, these are of low abundance. The appearance of these substituted cyclopropenium ions [$C_3F_2Cl^+$ and $C_3FCl_2^+$ in (I), $C_3F_2M^+$ in (II) and (III)] recalls the formation of $C_3H_3^+$ in the spectra of cyclopentadienylmetal compounds (see, for example, ref. 4), the only other type of five-membered carbocyclic metal complex investigated to date.

In general, the higher abundance and increased stability of the organorhenium ions over the corresponding manganese ions parallels the known relative thermal stability of the manganese and rhenium complexes. In particular, fission of the carbon–metal σ-bond occurs much less readily with the rhenium complex, as shown by the relative abundance of $C_5F_6Cl^+$, $M(CO)_5^+$ and $C_5F_6ClM(CO)_5^+$ (Mn: 24.5, 18 and 40; Re: 3, 6 and 92 %, respectively). Metastable peaks are observed, corresponding to some of the processes indicated in Chart 2, but in the case of these metal complexes, the majority of these transitions correspond to successive loss of CO groups from the parent ion.

EXPERIMENTAL

The complexes were obtained as described previously[1]. Mass spectra were obtained with an AEI MS9 double-focusing spectrometer, using an ionising potential of 70 V. Mass number determinations were made by calibration with perfluorotributylamine.

Assignments of peaks in the various spectra were aided by the appearance of characteristic multiplets of appropriate ions, due to $^{35}Cl_2$, $^{35}Cl^{37}Cl$ and $^{37}Cl_2$ (in $C_5F_6Cl_2$), ^{35}Cl and ^{37}Cl (complex II) and $^{35}Cl^{185}Re$, $^{35}Cl^{187}Re$ and $^{37}Cl^{185}Re$, and $^{37}Cl^{187}Re$ (complex III). The isotopic patterns observed agreed with those calculated from the known isotopic abundances.

TABLE 1

RELATIVE ABUNDANCES OF CARBONYL-CONTAINING FRAGMENTS

Ion	*Mn*	*Re*	*Ion*	*Mn*	*Re*	*Ion*	*Mn*	*Re*
$C_5F_6ClM(CO)_5^+$	40	92	$C_5F_5ClM(CO)_5^+$	7	17	$C_5F_6M(CO)_2^+$	0	4
$C_5F_6ClM(CO)_4^+$	0	19	$C_5F_5ClM(CO)_4^+$	10	8	$C_5F_6M(CO)_1^+$	0	3
$C_5F_6ClM(CO)_3^+$	7	47	$C_5F_5ClM(CO)_3^+$	2	2	$C_5F_6M(CO)_0^+$	0	52
$C_5F_6ClM(CO)_2^+$	39	64	$C_5F_5ClM(CO)_2^+$	6	5			
$C_5F_6ClM(CO)_1^+$	27	100	$C_5F_5ClM(CO)_1^+$	3	3			
$C_5F_6ClM(CO)_0^+$	204	80	$C_5F_5ClM(CO)_0^+$	8	7			

Table 1 summarises the relative abundances of the carbonyl containing ions from the metal complexes, and Table 2 lists the metastable peaks observed and their origins.

TABLE 2

METASTABLE PEAKS

m/e Observed	*m/e* Calculated	*Process*
$C_5F_6Cl_2$[a]		
68.0	67.9	$C_4F_3Cl_2^+ \rightarrow C_3F_2Cl^+ + CFCl$
80.5	80.6	$C_4F_4Cl_2^+ \rightarrow C_3FCl_2^+ + CF_3$
85.1	84.9	$C_4F_3Cl^+ \rightarrow C_3F_2Cl^+ + CF$
123.2	123.2	$C_4F_4Cl^+ \rightarrow C_4F_3Cl^+ + F$
125.5	125.5	$C_5F_6Cl_2^+ \rightarrow C_4F_3Cl_2^+ + CF_3$
127.4	127.3	
	129.2	
136.1	136.1	$C_5F_5Cl_2^+ \rightarrow C_4F_3Cl_2^+ + CF_2$
138.0	138.0	
	140.0	
	177.5 ($^{35}Cl^{37}Cl-^{37}Cl$)	$C_5F_6Cl_2^+ \rightarrow C_5F_6Cl^+ + Cl$
	179.0 ($^{35}Cl_2-^{35}Cl$)	
179.1	179.5 ($^{37}Cl_2-^{37}Cl$)	
181.0	181.0 ($^{35}Cl^{37}Cl-^{35}Cl$)	
$C_5F_6ClMn(CO)_5$[b]		
36.4	36.4	$Mn(CO)^+ \rightarrow Mn^+ + CO$
84.9	84.9	$C_4F_3Cl^+ \rightarrow C_3F_2Cl^+ + CF$
85.6	85.6	$C_4F_3ClMn^+ \rightarrow C_3F_2Mn^+ + CFCl$
101.9	101.5	$C_3F_2ClMn^+ \rightarrow C_3F_2Mn^+ + Cl$
104.9	104.0	$C_4F_3Mn^+ \rightarrow C_3F_2Mn^+ + CF$
108.2	108.2	$C_5F_6ClMn(CO)_5^+ \rightarrow C_5F_6Cl^+ + Mn(CO)_5$
120.9	121.0	$C_5F_6Cl^+ \rightarrow C_4F_4Cl^+ + CF_2$
123.8	123.5	$C_5F_5ClMn^+ \rightarrow Mn^+ + C_5F_5Cl$
143.0	143.0	$C_4F_4Mn^+ \rightarrow C_4F_3Mn^+ + F$
154.9	155.2	$C_5F_5ClMn^+ \rightarrow C_4F_3ClMn^+ + CF_2$
165.7	165.5	$C_5F_6ClMn^+ \rightarrow C_5F_6Cl^+ + Mn$
172.4	172.8	$C_5F_6Cl^+ \rightarrow C_5F_5Cl^+ + F$
198.1	198.6	$C_5F_6ClMn^+ \rightarrow Mn^+ + C_5F_6Cl$
228.8	227.4	$C_5F_6ClMn^+ \rightarrow C_5F_5ClMn^+ + F$
	229.5	
238.8	238.7	$C_5F_6ClMn(CO)^+ \rightarrow C_5F_6ClMn^+ + CO$
240.8	240.7	
266.5	266.5	$C_5F_6ClMn(CO)_2^+ \rightarrow C_5F_6ClMn(CO)^+ + CO$
294.1	294.4	$C_5F_6ClMn(CO)_3^+ \rightarrow C_5F_6ClMn(CO)_2^+ + CO$
296.1	296.4	
303.1	303.4	$C_5F_5ClMn(CO)_4^+ \rightarrow C_5F_5ClMn(CO)_3^+ + CO$
331.2	331.2	$C_5F_5ClMn(CO)_5^+ \rightarrow C_5F_5ClMn(CO)_4^+ + CO$
333.0	333.1	
336.2	337.0	$C_5F_6ClMn(CO)_5^+ \rightarrow C_5F_6Mn(CO)_5^+ + Cl$
352.0	352.0	$C_5F_6{}^{37}ClMn(CO)_5^+ \rightarrow C_5F_6{}^{37}ClMn(CO)_4^+ + CO$
$C_5F_6ClRe(CO)_5$[c]		
268.1	268.0	$C_5F_6ClRe^+ \rightarrow C_4F_3ClRe^+ + CF_3$
327.2	327.0	$C_5F_6ClRe(CO)^+ \rightarrow C_5F_6Re(CO)^+ + Cl$
329.0	329.0	

(continued on next page)

TABLE 2 (*continued*)

m/e *Observed*	*m/e* *Calculated*	*Process*
367.5	368.0	$C_5F_6ClRe(CO)^+ \rightarrow C_5F_6ClRe^+ + CO$
369.5	370.0	
	371.9	
376.8	376.9	$C_5F_5ClRe(CO)_2^+ \rightarrow C_5F_5ClRe(CO)^+ + CO$
395.8	396.0	$C_5F_6ClRe(CO)_2^+ \rightarrow C_5F_6ClRe(CO)^+ + CO$
397.8	398.0	
399.9	400.0	
424.0	423.6	$C_5F_6ClRe(CO)_3^+ \rightarrow C_5F_6ClRe(CO)_2^+ + CO$
	425.5	
426.2	427.7	
451.0	451.4	$C_5F_6ClRe(CO)_4^+ \rightarrow C_5F_6ClRe(CO)_3^+ + CO$
453.0	453.2	
	455.4	
460.0	460.5	$C_5F_5ClRe(CO)_5^+ \rightarrow C_5F_5ClRe(CO)_4^+ + CO$
462.0	462.5	
	464.5	
479.0	479.5	$C_5F_6ClRe(CO)_5^+ \rightarrow C_5F_6ClRe(CO)_4^+ + CO$
481.0	481.6	
	483.6	

[a] Single values are calculated for $^{35}Cl_2$; three values are calculated for the combinations $^{35}Cl_2$, $^{35}Cl^{37}Cl$ and $^{37}Cl_2$. [b] Unless otherwise stated, single values for chlorine-containing peaks are calculated for ^{35}Cl. [c] Single values are calculated for the combination $^{35}Cl^{187}Re + ^{37}Cl^{185}Re$; three values are for all possible combinations.

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SUMMARY

The mass spectra of the chlorofluorocarbon $C_5F_6Cl_2$, and the derived complexes $C_5F_6ClM(CO)_5$ (M = Mn and Re), are reported, and plausible fragmentation schemes are discussed.

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