

## COMPARATIVE MASS SPECTROMETRIC INVESTIGATION OF TRANSITION METAL POLYMETHYLCYCLOPENTADIENYLCARBONYL COMPLEXES

### I. MASS SPECTRA OF $R_nC_5H_{5-n}Re(CO)_3$ ( $R = CH_3$ , $n = 0-5$ ; $R = t-C(CH_3)_3$ , $n = 1$ )

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#### Summary

Mass spectra of  $\pi-(CH_3)_nC_5H_{5-n}Re(CO)_3$  ( $Me_nCpReT$ ) ( $n = 0-5$ ) and  $t-BuCpReT$  were recorded, from which it was found that molecular ion ( $M^+$ ) fragmentation for  $Me_nCpReT$  ( $n = 0, 1$ ) differs from that for  $Me_nCpReT$  ( $n = 2-5$ ). The  $(M - 2CO)^+$  ions have maximum intensity in  $n = 0, 1$  complexes, and the  $(M - 2CO - H_2)^+$  ions, in  $n = 2-5$  complexes.  $H_2$  elimination from  $(M - 2CO)^+$  is typical of rhenium  $\pi$ -cyclopentadienyl complex fragmentation, where the number of methyl groups in the Cp ring is  $> 1$ , and seems to occur with participation of the Re atom.

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Transition metal  $\pi$ -complex chemistry studied in the gas phase requires a greater number of structure-diversified complexes for investigation. In this respect, a comparative mass spectrometric study of similar transition-metal complexes as a function of metal location in periodic table is of particular importance. Here we deal with mass spectrometric investigation of methyl homologues of rhenium cyclopentadienyltricarbonyl ( $Me_nCpReT$ ) ( $n = 0-5$ ). Mass spectra of rhenium tricarbonyl complexes have so far been insufficiently studied [1,2]. This work in particular is intended (i) to study the unique features of ( $M^+$ ) molecular ion mass spectrometric fragmentation in  $Me_nCpReT$ , and (ii) to elucidate the effect of spatial interactions on fragmentation nature. Moreover, a certain positive charge com-

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TABLE 1

INTENSITIES (AT 70 eV) OF Re-CONTAINING IONS IN THE MASS SPECTRA OF  $R_nC_5H_{5-n}Re(CO)_3$  ( $R = CH_3$ ,  $n = 0-5$ ;  $R = t$ -butyl,  $n = 1$ )

Ion	n						Bu <sup>t</sup> *
	5	4	3	2	1	0	
$M^+$	50	55	54	52	69	56	100
$(M-CO)^+$	41	39	35	39	27	18	20
$(M-CO-H_2)^+$	24	13	10	4	-	-	50
$(M-2CO)^+$	17	22	33	80	100	100	81
$(M-2CO-H_2)^+$	100	100	100	100	2	-	35
$(M-3CO)^+$	-	1.5	8	23	54	50	-
$(M-3CO-H_2)^+$	16	21	33	76	31	19	15
$(M-3CO-2H_2)^+$	12	14	26	26	15	6	31
$(M-3CO-3H_2)^+$	10	18	20	3	-	-	31
$(M-3CO-4H_2)^+$	8	11	4	4	-	-	12
$(M-3CO-5H_2)^+$	6	1	-	-	-	-	-
$C_8H_7Re^+$	8	-	-	-	-	-	14
$C_8H_6Re^+$	-	1.5	-	-	-	-	11
$C_8H_5Re^+$	8	2	-	-	-	-	10
$C_8H_3Re^+$	4	-	-	-	-	-	4
$C_7H_7Re^+$	4	-	-	-	-	-	6
$C_7H_6Re^+$	3	-	-	-	-	-	-
$C_7H_5Re^+$	5	9	2	-	-	-	11
$C_7H_4Re^+$	5	6	2	-	-	-	-
$C_6H_6Re^+$	-	-	3	-	-	-	-
$C_6H_5Re^+$	7	3	15	3	-	-	4
$C_6H_4Re^+$	8	4	14	7	-	-	12
$C_6H_3Re^+$	4	2	10	7	-	-	6
$C_6H_2Re^+$	3	1.5	2	2	-	-	6
$C_5H_5Re^+$	-	4	2	20	1.5	-	6
$C_5H_4Re^+$	4	5	4	20	-	-	-
$C_5H_3Re^+$	5	6	5	41	1.5	-	15
$C_5H_2Re^+$	2	2	3	17	-	-	-
$C_5HRe^+$	2	2	3	17	2	-	9
$C_4H_5Re^+$	-	1	2	4	4	-	1.5
$C_4H_4Re^+$	6	2	4	8	3	-	1.5
$C_4H_3Re^+$	6	3	8	9	15	1.5	6
$C_4H_2Re^+$	3	2	4	10	3	-	1.5
$C_4HRe^+$	3	4	5	-	3	2	6
$C_3H_3Re^+$	3	2.5	6	22	1.5	9	6
$C_3H_2Re^+$	10	6	11	48	4	11	12
$C_3HRe^+$	6	4	12	44	7	23	9
$C_2H_3Re^+$	2	1.5	3	11	4	-	1.5
$C_2H_2Re^+$	6	2	7	20	6	-	4
$C_2HRe^+$	4	2	5	3	9	6	3
$CH_2Re^+$	-	1	2	11	-	1	-
$CHRe^+$	4	3	8	33	4	15	8
$CRe^+$	-	1	2	15	2	6	-
$HRe^+$	6	-	2	9	1.5	1.5	-
$Re^+$	10	6	14	61	15	12.5	12
$M^{2+}$	3	-	4	3	3	3	-
$(M-CO)^{2+}$	-	-	1.5	4	6	3	-

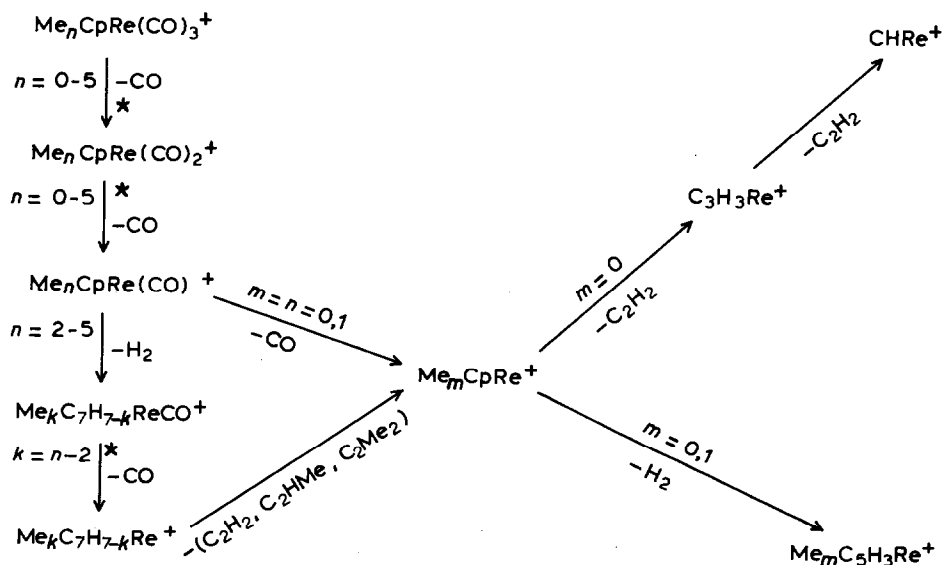
TABLE 1 (continued)

Ion	<i>n</i>						Bu <sup>†</sup> *
	5	4	3	2	1	0	
( <i>M</i> - CO - H) <sup>2+</sup>	-	10	11	13	-	-	-
( <i>M</i> - 2CO) <sup>2+</sup>	-	-	-	-	7	5	-
( <i>M</i> - 2CO - H) <sup>2+</sup>	-	11	9	-	7	-	-
( <i>M</i> - 2CO - H <sub>2</sub> ) <sup>2+</sup>	7	-	2	-	-	-	-
( <i>M</i> - 3CO) <sup>2+</sup>	-	-	-	-	7	12.5	-
( <i>M</i> - 3CO - H) <sup>2+</sup>	-	10	10	-	11	2	-
( <i>M</i> - 3CO - H <sub>2</sub> ) <sup>2+</sup>	8	5	6	-	7	-	-
( <i>M</i> - 3CO) - 2H <sub>2</sub> ) <sup>2+</sup>	5	2	-	-	-	-	-
( <i>M</i> - CO - CH <sub>3</sub> ) <sup>2+</sup>	-	-	-	-	-	-	4.5
( <i>M</i> - 2CO - CH <sub>4</sub> - H) <sup>2+</sup>	-	-	-	-	-	-	11

\* *t*-Butyl CpRe(CO)<sub>3</sub> mass spectrum contains, besides the above-mentioned fragment ions, the ions; (*M* - CH<sub>3</sub>)<sup>+</sup> - 16%, (*M* - CO - CH<sub>3</sub>)<sup>+</sup> - 12%, (*M* - CO - CH<sub>3</sub> - H<sub>2</sub>)<sup>+</sup> - 10%, (*M* - 2CO - CH<sub>4</sub> - H<sub>2</sub>)<sup>+</sup> - 30%, (*M* - 2CO - CH<sub>4</sub>)<sup>+</sup> - 42%.

penetration on the metal ion is expected to occur in the molecular ions resulting in their stabilization with the accumulation of electron-donor methyl groups in the cyclopentadienyl ring.

Table 1 lists molecular (*M*<sup>+</sup>) and fragment ions observed in the mass spectra of the compounds under study together with their relative intensities (100% refers to the ion with maximum intensity). The data show that these molecular ions undergo successive elimination of three carbonyl ligands, this is confirmed by the corresponding metastable peaks (Table 2). On the other hand, fragmentation pathways associated with the cyclopentadienyl ligand or its fragment elimination, while preserving metal carbonyl fragments, are not observed. Table 1 also shows that the mass spectra are characterized by a vast amount of completely decarbonylated



SCHEME 1. Primary fragmentation of the molecular ions of  $\text{Me}_n \text{C}_5 \text{H}_{5-n} \text{Re}(\text{CO})_3$ ,  $n = 0-5$  (70 eV).

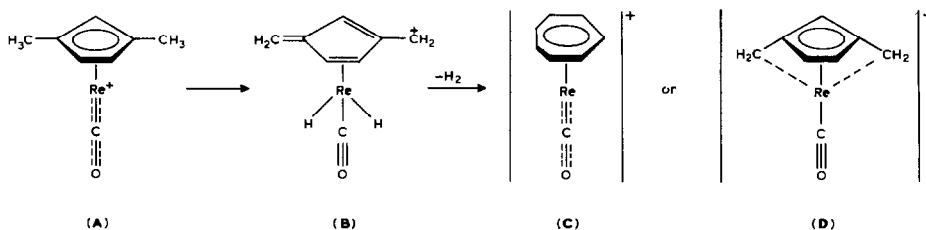
Re-containing fragment ions. This feature is not observed in the mass spectra of 1st row transition metal cyclopentadienyl carbonyl complexes (Mn, Co, Cr) [1,3-7] but is found in Mo and W complexes [1,4]. One can assume that this is due to a stronger Re-Cp or Re-cyclopentadienyl ligand bond which remains intact during the entire ligand fragmentation (Scheme 1).

Molecular ion ( $M^+$ ) intensity values show that these ions are sufficiently stable for all members of the series. With the emergence of the first R group (R = methyl or t-butyl) in the cyclopentadienyl ring, ( $M^+$ ) molecular ion intensities ( $J$ ) increase (by 70% in MeCpReT, and by 100% in t-BuCpReT), probably owing to both positive charge compensation on the metal atom by donor alkyl groups and to an increase in vibrational degrees of freedom. Further increases in the methyl substitution value ( $n$ ) had no effect on the predicted molecular ion ( $M^+$ ) stabilization: Me<sub>*n*</sub>CpReT ( $n = 2-5$ ) molecular ion intensity is approximately similar to that of CpReT itself. However, ( $M - CO$ )<sup>+</sup> ion intensities increase with  $n$ . These observations may be attributed to both methyl group electron-donor characteristics and to an increase in spatial methyl-CO group interactions in ( $M^+$ ) molecular ions with increasing  $n$ , which contributes to more facile ( $M - CO$ )<sup>+</sup> ion formation (with large  $n$ ) and simultaneous destabilization of their  $M^+$  ions.

Beside decarbonylation, dehydrogenation is also important for ion fragmentations, in particular for ( $M - 2CO - H_2$ )<sup>+</sup> ion formation which appears even before the last carbonyl group is eliminated. From this aspect the complexes under study can be divided into two groups. For CpReT and MeCpReT ( $n = 0, 1$ ), ( $M - 2CO$ )<sup>+</sup> ion dehydrogenation shows a negligible contribution to total ionic current. However, ( $M - 2CO$ )<sup>+</sup> ion dehydrogenation becomes predominant with  $n = 2-5$ . It should be emphasized that ( $M - 2CO - H_2$ )<sup>+</sup> ions are have the greatest intensity in the Me<sub>*n*</sub>CpReT ( $n = 2-5$ ) spectra. We assume that the maximum intensity of these ions (with  $n = 2-5$ ), and the dehydrogenation which occurs in the presence of the third carbonyl group in the ( $M - 2CO$ )<sup>+</sup> ions, to be accounted for by prevalence of the metal during dehydrogenation. Deep dehydrogenation of fragment ions which takes place after the third carbonyl group is eliminated and results in a preponderance of Re-containing ions in the mass spectra (Table 1), can also be explained by an active Re contribution to dehydrogenation. Such behaviour during mass spectrometric fragmentation of the present complexes conforms to the catalytic properties of some Re compounds [8] in the dehydrogenation and dehydrocyclization reactions reported earlier [9]. The significance of the Re atom is shown by apparent H<sub>2</sub> elimination of the metal-hydride particle (**B**). Thus particle formation is possible

TABLE 2  
METASTABLE IONS ( $m^*$ ) IN THE MASS SPECTRA OF Me<sub>*n*</sub>C<sub>5</sub>H<sub>5-*n*</sub>(Re(CO)<sub>3</sub>),  $n = 0-5$

Process	$m^*$					
	5	4	3	2	1	0
$M^+ \rightarrow (M - CO)^+ + CO$	-	-	-	-	296.2	282.5
$(M - CO - H_2)^+ \rightarrow (M - CO - 2H_2)^+ + H_2$	-	358	344	-	-	-
$(M - 2CO - H_2)^+ \rightarrow (M - 2CO - 2H_2)^+ + H_2$	-	-	-	302	-	-
$(M - CO)^+ \rightarrow (M - 2CO)^+ + CO$	324	310	296.2	282.3	268.5	254.5
$(M - 2CO - H_2)^+ \rightarrow (M - 3CO - H_2)^+ + CO$	294.2	280.3	266.4	-	-	-



SCHEME 2

when two conditions are satisfied viz: (i) presence of two free coordination sites in metal, i.e. following two carbonyl ligand eliminations, and (ii) occurrence of two methyl groups in cyclopentadienyl ring. Therefore it is clear that  $(M-2CO)^+$  ions with  $n=0, 1$  are incapable of hydrogen elimination, however, in the mono-*t*-butyl substituted complex with three methyl groups, dehydrogenation is possible since the  $(M-2CO-H_2)^+$  ion intensity is rather high (35%). Dehydrogenation seems to be a kinetic destabilization factor for  $(M-2CO)^+$  ions (with increased  $n$ ) as well. These ions show maximum intensities when  $n=0, 1$ , while with  $n=2-5$  the intensities decrease in large steps with increase in  $n$ , from 80% in  $Me_2CpReT$  to 17% in  $Me_5CpReT$ . The maximum intensities of  $(M-2CO-H_2)^+$  with  $n=2-5$  and of  $(M-2CO)^+$  with  $n=0, 1$  indicate that the corresponding structures are very stable. For  $(M-2CO-H_2)^+$  ions (with empirical formulae of  $(Me_kC_7H_{7-k}ReCO)^+$ , where  $k=0-3$  for  $n=2-5$ , respectively) this stabilization may be related to the formation of a ligand tropylium system (C) resulting in stabilization owing to high positive charge delocalization on the organic ligand and to the increase in metal coordination number (Scheme 2). Relatively high intensities of  $C_5H_5Re$  (20%),  $C_3H_3Re$  (22%), and  $CHRe$  (33%) fragment ions, obtained from  $C_7H_7Re$  (76%) fragmentation (with  $n=2$ ) by successive acetylene molecule eliminations, seems to confirm indirectly such a structure. However, structure D cannot be avoided. As for the maximum  $(M-2CO)^+$  ion intensities with  $n=0, 1$ , they could also be attributed to linear structure A emergence where interaction of Re *d*-orbitals with the remaining vacant carbonyl group  $\pi^*$ -orbitals can be maximal, leading to additional strengthening of the last Re-CO bond. It is also noteworthy that the mass spectra of the complexes under study include a large amount of double-charged metal-containing ions, typical of the strong 5*d* transition metal complexes [1,4].

The compounds were obtained by a published method [10]. Mass spectra were measured on a CH-8 Varian MAT instrument with an ionization potential of 70 eV and an ion source temperature of 150 °C.

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