Journal of Organometallic Chemistry, 94 (1975) 425—440

MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

III*. MASS SPECTRA OF SOME π-CYCLOPENTADIENYL COMPLEXES OF SEVEN—COORDINATE RHENIUM

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(Received March 2nd, 1975)

Summary

The mass spectra of π-$RC_5H_4Re(CO)_2XY$ (R = H, CH_3, $COOCH_3$, X, Y = H, CH_3, $COCH_3$, Br, I, HgCl) have been studied. A successive expulsion of carbonyl groups, a common fragmentation path for cyclopentadienyl metal carbonyls, is observed in addition to the parallel elimination of substituents X and Y from the molecular ions of seven-coordinate rhenium complexes. Loss of a hydrogen molecule from the $[M - 2CO]^+$ ion is a characteristic of the fragmentation of σ-methyl complexes.

Recently we reported the synthesis of certain π-cyclopentadienyl complexes of seven-coordinate rhenium [1]. The main fragmentation paths under electron impact are now considered for the compounds of general formula π-$RC_5H_4Re(CO)_2XY$; namely π-$C_5H_5Re(CO)_2(CH_3)_2$, π-$C_5H_5Re(CO)_2Br(CH_3)$, π-$C_5H_5Re(CO)_2 \cdot I(CH_3)$, π-$C_5H_5Re(CO)_2I(COCH_3)$, π-$C_5H_5Re(CO)_2Br_2$, π-$C_5H_5Re(CO)_2BrH$, π-$C_5H_5Re(CO)_2IH$, π-$C_5H_5Re(CO)_2I(HgCl)$, π-$(CH_3C_5H_4)Re(CO)_2Br_2$, π-$(CH_3OOC\text{-}C_5H_4)Re(CO)_2Br_2$ and π-$IC_5H_4Re(CO)_2Br_2$.

The calculated monoisotopic** spectra of the above compounds, as well as the metastable transitions observed are represented in the Tables 1-10. A relatively high stability of the molecular ions of all complexes permits an unambiguous determination of the molecular weights of such compounds.

A successive expulsion of both carbonyl groups resulting in formation of the ions $[RC_5H_4ReXY]^+$ is a typical feature for all complexes studied except π-$C_5H_5Re(CO)_2(CH_3)_2$ and π-$C_5H_5Re(CO)_2I(HgCl)$. Most cyclopentadienyl metal carbonyls of the type $C_5H_5M(CO)_nX_m$ (where X is a σ-bonded ligand Ar, Alk,

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* Part I. The influence of σ-bonded ligands on the fragmentation of π-allyl derivatives of iron carbonyl [2]. Part II. Mono- and di-cyclopentadienyl derivatives of titanium [3].

** The intensities are corrected by an isotopic composition of C, Cl, Br, Re and Hg.

(continued on p. 434)

TABLE 1

MASS SPECTRUM OF $C_5H_5Re(CO)_2(CH_3)_2$

Ion	m/e	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	338	62	56	100
$M-CH_3{}^+$	323	12	11	14
$M-CO^+$	310	47	49	92
$C_6H_5Re(CO)(CH_3)^+$	308	10	10	12
$C_7H_7Re(CO)^+$	306	16	17	16
$M-CH_3-CO^+$	295	21	21	10
$M-CO-CH_4{}^+$	294	68	74	69
$C_6H_6Re(CO)^+$	293	75	64	
$C_5H_5Re(CO)^+$	280	8	8	
$C_5H_4Re(CO)^+$	279	4	3	
$C_7H_7Re^+$	278	24	22	
$C_7H_6Re^+$	277	4	4	
$C_7H_5Re^+$	276	5	7	
$M-CO-CH_3-CO^+$	267	2	1	
$C_6H_7Re^+$	266	100	100	3
$C_6H_6Re^+$	265	54	50	
$C_6H_5Re^+$	264	22	18	
$C_6H_4Re^+$	263	41	22	
$C_6H_3Re^+$	262	8	4	
$C_5H_5Re^+$	252	21	14	
$C_5H_4Re^+$	251	4		
$C_5H_3Re^+$	250	10	3	
C_5HRe^+	248	4		
$C_4H_4Re^+$	239	12	3	
$C_4H_3Re^+$	238	10	1	
$C_4H_2Re^+$	237	6		
C_4HRe^+	236	4		
$C_3H_3Re^+$	226	7	1	
$C_3H_2Re^+$	225	11		
C_3HRe^+	224	10		
$C_2H_2Re^+$	213	14		
C_2HRe^+	212	11		
$CHRe^+$	200	8		
CRe^+	199	2		
Re^+	187	10		
M^{2+}	169	2		
$M-CH_3{}^{2+}$	161.5	2		
$C_6H_6Re(CO)(CH_3)^{2+}$	154	3		
$C_7H_7Re(CO)^{2+}$	153	7		
$M-CO-CH_4{}^{2+}$	147	12		
$C_6H_6Re(CO)^{2+}$	146.5	8		
$C_7H_7Re^{2+}$	139	10		
$C_6H_7Re^{2+}$	133	14		
$C_6H_6Re^{2+}$	132.5	7		
$C_6H_5Re^{2+}$	132	14		

(continued)

TABLE 1 (continued)

Metastable transitions

m/e	Process	Neutral fragment lost
304	$308 \rightarrow 306 + 2$	H_2
284	$338 \rightarrow 310 + 28$	CO
279	$310 \rightarrow 294 + 16$	CH_4
269	$323 \rightarrow 295 + 28$	CO
254	$308 \rightarrow 280 + 28$	CO
252	$306 \rightarrow 278 + 28$	CO
240	$294 \rightarrow 266 + 28$	CO
	$265 \rightarrow 252 + 13$	CH
226	$280 \rightarrow 252 + 28$	CO
	$252 \rightarrow 239 + 13$	CH
213	$239 \rightarrow 226 + 13$	CH
200	$226 \rightarrow 213 + 13$	CH
187	$213 \rightarrow 200 + 13$	CH
120	$294^{2+} \rightarrow 266^{2+} + CO$	

TABLE 2

MASS SPECTRUM OF $C_5H_5Re(CO)_2Br(CH_3)$

Ion	*m/e*	Rel. intensity 50 eV
M^+	402	64
$M-CH_3^+$	387	9
$M-CO^+$	374	96
$M-CH_3-CO^+$	359	16
$M-2CO^+$	346	71
$M-2CO-H_2^+$	344	100
$M-2CO-2H_2^+$	342	27
$C_5H_5ReBr^+$	331	74
$C_5H_3ReBr^+$	329	14
C_5HReBr^+	327	6
$M-Br^+$	323	5
$C_4H_4ReBr^+$	318	10
$C_4H_3ReBr^+$	317	6
$C_4H_2ReBr^+$	316	3
$M-Br-CH_3^+$	308	8
$C_3H_3ReBr^+$	305	33
C_3HReBr^+	303	8
$M-Br-CO^+$	295	5
$C_6H_6Re(CO)^+$	293	17
$C_2H_2ReBr^+$	292	8
$C_5H_5Re(CO)^+$	280	14
$CHReBr^+$	279	6
$C_6H_6Re^+$	265	23
$C_6H_5Re^+$	264	14
$C_6H_4Re^+$	263	9
$C_5H_5Re^+$	252	13
$C_5H_3Re^+$	250	2
$C_4H_4Re^+$	239	5
$C_4H_3Re^+$	238	6
$C_3H_3Re^+$	226	3
$C_3H_2Re^+$	225	6
C_3HRe^+	224	6
$C_2H_2Re^+$	213	3
C_2HRe^+	212	1
$CHRe^+$	200	2

TABLE 3

MASS SPECTRUM OF $C_5H_5Re(CO)_2I(CH_3)$

Ion	m/e	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	450	100	100	100
$M-CH_3^+$	435	21	22	9
$M-CO^+$	422	80	88	55
$M-CH_3-CO^+$	407	17	18	
$M-2CO^+$	394	40	49	9
$M-2CO-H_2^+$	392	65	67	3
$M-2CO-2H_2^+$	390	32	20	2
$C_5H_5ReI^+$	379	56	56	2
$C_5H_3ReI^+$	377	18	16	
$C_4H_4ReI^+$	366	5	4	
$C_4H_3ReI^+$	365	4		
$C_4H_2ReI^+$	364	2		
C_4HReI^+	363	1		
$C_3H_3ReI^+$	353	20	11	
$C_3H_2ReI^+$	352	7		
C_3HReI^+	351	13	3	
C_2HReI^+	339	4	2	
C_2ReI^+	338	3		
$CHReI^+$	327	10		
$M-I^+$	323	2	2	1
$M-HI^+$	322	2	2	1
ReI^+	314	4		
$M-I-CH_3^+$	308	5	5	2
$M-I-CO^+$	295	5	4	
$C_6H_7Re(CO)^+$	294	3	2	
$C_6H_6Re(CO)^+$	293	22	28	1
$C_5H_5Re(CO)^+$	280	7	7	
$C_6H_7Re^+$	266	9	8	
$C_6H_6Re^+$	265	20	22	2
$C_6H_5Re^+$	264	6	4	
$C_6H_4Re^+$	263	16	12	
$C_5H_5Re^+$	252	8	7	
$C_5H_3Re^+$	250	5	2	
$C_4H_4Re^+$	239	5	2	
$C_4H_3Re^+$	238	7	3	
$C_4H_2Re^+$	237	2		
$C_3H_3Re^+$	226	4		
$C_3H_2Re^+$	225	11		
C_3HRe^+	224	11		
$C_2H_2Re^+$	213	4		
C_2HRe^+	212	5		
$CHRe^+$	200	7		
ReH_2^+	189	8		
ReH^+	188	7		
Re^+	187	4		
I^+	127	5	3	

TABLE 4

MASS SPECTRUM OF $C_5H_5Re(CO)_2I(COCH_3)$

Ion	*m/e*	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	478	30	38	86
$M-CH_3^+$	463	2	2	3
$M-CO^+$	450	18	22	79
$M-COCH_3^+$	435	20	23	31
$M-2CO^+$	422	12	14	28
$C_5H_5Re(CO)I^+$	407	29	33	13
$C_6H_8ReI^+$	394	6	8	10
$C_6H_6ReI^+$	392	22	25	6
$C_6H_4ReI^+$	390	7	8	
$C_5H_5ReI^+$	379	76	89	6
$C_5H_3ReI^+$	377	22	22	
C_5HReI^+	375	4	4	
$C_4H_4ReI^+$	366	2	2	
$C_4H_3ReI^+$	365	2	2	
$C_4H_2ReI^+$	364	2	2	
C_4HReI^+	363	1	1	
$C_3H_3ReI^+$	353	26	22	2
$M-I^+$, C_3HReI^+	351	20	16	31
$C_2H_2ReI^+$	340	2	2	
$C_5H_5Re(CO)_3^+$	336	50	51	100
$CHReI^+$	327	2	2	
$C_5H_5Re(CO)(COCH_3)^+$	323	9	11	7
$C_5H_3Re(CO)(COCH_3)^+$	321	10	12	11
$C_5H_5Re(CO)_2^+$	308	36	43	37
$C_5H_5Re(COCH_3)^+$	295	18	22	6
$C_5H_3Re(COCH_3)^+$	293	29	38	3
$C_5H_5Re(CO)^+$	280	100	100	15
$C_3H_3Re(COCH_3)^+$	269	7	10	
$C_5H_5Re(CH_3)^+$	267	3	2	
$C_6H_6Re^+$	265	17	22	
$C_6H_4Re^+$	263	9	10	
$C_5H_5Re^+$	252	73	75	2
$C_5H_3Re^+$	250	28	28	
C_5HRe^+	248	12	3	
$C_4H_4Re^+$	239	4	3	
$C_4H_3Re^+$	238	5	2	
$C_3H_3Re^+$	226	26	19	
$C_3H_2Re^+$	225	36	9	
C_3HRe^+	224	42	11	
$C_2H_2Re^+$	213	5	1	
C_2HRe^+	212	9	1	
HI^+	128	31	36	31
I^+	127	19	18	

(continued)

TABLE 4 (continued)

Metastable transitions

m/e	Process	Neutral fragment lost
424	478 → 450 + 28	CO
396	478 → 435 + 43	$COCH_3$
	450 → 422 + 28	CO
381	435 → 407 + 28	CO
368	422 → 394 + 28	CO
353	407 → 379 + 28	CO
297	351 → 323 + 28	CO
282	336 → 308 + 28	CO
269	323 → 295 + 28	CO
258	478 → 351 + 127	I
254	308 → 280 + 28	CO
227	280 → 252 + 28	CO

TABLE 5

MASS SPECTRUM OF $C_5H_5Re(CO)_2Br_2$

Ion	*m/e*	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	468	13	5	15
$M-CO^+$	440	25	15	32
$M-2CO^+$	412	49	33	14
$M-Br$	387	30	28	100
$M-Br-CO^+$	359	23	28	33
$ReBr_2^+$	347	3		
$C_5H_5ReBr^+$	331	100	100	18
$C_5H_3ReBr^+$	329	23	15	3
$C_5H_5Re(CO)_2^+$	308	9	9	7
$C_5H_3Re(CO)_2^+$	306	8	6	1
$C_3H_3ReBr^+$	305	30	14	2
$C_3H_2ReBr^+$	304	16	4	
C_3HReBr^+	303	16	8	
$C_5H_5Re(CO)^+$	280	33	27	2
$CHReBr^+$	279	10		
$ReBr^+$	266	3		
$C_5H_5Re^+$	252	21	17	2
$C_5H_3Re^+$	250	9	6	
C_5HRe^+	248	5		
$C_3H_3Re^+$	226	11	3	
$C_3H_2Re^+$	225	11	3	
C_3HRe^+	224	25	6	
C_3Re^+	223	2		
HBr^+	80	34	53	
Br^+	79	15	18	

Metastable transitions

m/e	Process	Neutral fragment lost
414	468 → 440 + 28	CO
386	440 → 412 + 28	CO
254	308 → 280 + 28	CO
227	280 → 252 + 28	CO

TABLE 6

MASS SPECTRA OF $C_5H_5Re(CO)_2(X)H$ (50 eV)

Ion	X = Br		X = I	
	m/e	Rel. intensity	m/e	Rel. intensity
M^+	388	19	436	13
$M - CO^+$	360	31	408	15
$M - 2CO^+$	332	50	380	15
$M - 2CO - H^+$	331	19	379	11
$M - 2CO - C_2H_2^+$	306	6	354	5
$C_3H_3ReX^+$	305	4	353	6
$C_5H_5Re(CO)_3^+$	336	66	336	68
$C_5H_5Re(CO)_2^+$	308	33	308	35
$C_5H_5Re(CO)^+$	280	100	280	100
$C_5H_5Re^+$	252	57	252	60
$C_5H_3Re^+$	250	11	250	20
$C_3H_3Re^+$	226	6	226	14
C_3HRe^+	224	3	224	20
$CHRe^+$	200		200	8
HX^+	80	5	128	7

TABLE 7

MASS SPECTRUM OF $C_5H_5Re(CO)_2I(HgCl)$

Ion	m/e	Rel. intensity 50 eV
M^+	672	
$M - HgCl^+$	435	31
$C_5H_5Re(CO)I^+$	407	38
$C_5H_5ReI^+$	379	59
$C_5H_3ReI^+$	377	14
$C_3H_3ReI^+$	353	16
$C_3H_2ReI^+$	352	6
C_3HReI^+	351	5
$C_5H_5Re(CO)_3^+$	336	56
$C_5H_5Re(CO)_2^+$	308	25
$C_5H_5ReCl^+$	287	28
$C_5H_3ReCl^+$	285	9
$C_5H_5Re(CO)^+$	280	100
$C_5H_5Re^+$	252	53
$C_5H_3Re^+$	250	16
$C_3H_3Re^+$	226	20
$C_3H_2Re^+$	225	23
C_3HRe^+	224	18
Hg^+	202	150
Re^+	187	25
HI^+	128	22
I^+	127	14

TABLE 8

MASS SPECTRUM OF $CH_3C_5H_4Re(CO)_2Br_2$

Ion	m/e	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	482	7	5	9
$M-CO^+$	454	22	19	31
$M-2CO^+$	426	44	44	14
$M-Br^+$	401	31	36	100
$M-Br-CO^+$	373	21	26	24
$CH_3C_5H_4ReBr^+$	345	98	100	17
$C_6H_6ReBr^+$	344	100	86	9
$C_6H_5ReBr^+$	343	59	59	3
$C_6H_4ReBr^+$	342	23	25	2
$C_6H_3ReBr^+$	341	4	7	1
$C_5H_5ReBr^+$	331	6	3	
$M-2Br^+$	322	3	5	
$CH_3C_3H_2ReBr^+$	319	3	4	
$CH_3C_3HReBr^+$	318	12	5	
$CH_3C_3ReBr^+$	317	40	19	
$C_3H_3ReBr^+$	305	6	2	
C_3HReBr^+	303	4		
$CH_3C_5H_4Re(CO)^+$	294	17	14	
$C_6H_6Re(CO)^+$	293	10		
$C_6H_5Re(CO)^+$	292	3	1	
$CHReBr^+$	279	3		
$CH_3C_5H_4Re^+$, $ReBr^+$	266	12	11	2
$C_6H_6Re^+$	265	10	10	1
$C_6H_5Re^+$	264	7	4	
$C_4H_3Re^+$	238	5		
C_4HRe^+	236	3		
$C_3H_2Re^+$	225	3		
C_3HRe^+	224	7		
$C_2H_2Re^+$	213	8		
C_2HRe^+	212	9		
Re^+	187	6		
$C_6H_6ReBr^{2+}$	172.5	11		
$C_6H_5ReBr^{2+}$	172	12		
HBr^+	80	71	90	
Br^+, $CH_3C_5H_4^+$	79	23	19	

Metastable transitions

m/e	Process	Neutral fragment lost
427	482 → 454 + 28	CO
399	454 → 426 + 28	CO
346	401 → 373 + 28	CO
277	426 → 344 + 82	HBr

TABLE 9

MASS SPECTRUM OF $CH_3OOCC_5H_4Re(CO)_2Br_2$

Ion	m/e	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	526	20	23	32
$M - CO^+$	498	45	53	100
$M - MeO^+$	495	3	3	
$M - 2CO^+$	470	100	100	25
$M - MeO - CO^+$	467	3	3	
$M - Br^+$	445	28	28	89
$M - 2CO - CH_2O^+$	440	10	14	
$M - 2CO - COCH_3^+$	427	30	19	
$M - Br - CO^+$	417	13	12	20
$C_5H_4ReBr_2^+$	411	11	3	
$M - Br - 2CO^+$	389	48	35	12
$CH_3OReBr_2^+$	378	9	5	
$M - 2Br^+$	366	4	4	
$CH_3OC_5H_4ReBr^+$	361	40	32	
$C_5H_4COReBr^+$	358	63	35	
$ReBr_2^+$	347	6		
$C_5H_4OReBr^+$	346	6	2	
$C_5H_3OReBr^+$	345	4	1	
$M - 2Br - CO^+$	338	1	2	
$C_5H_5ReBr^+$	331	64	30	
$C_5H_4ReBr^+$	330	19	7	
$C_5H_3ReBr^+$	329	31	4	
C_5HReBr^+	327	4		
$C_4H_6ReBr^+$	320	17	2	
$M - 2Br - 2CO^+$	310	31	21	
$C_3H_3ReBr^+$	305	21	2	
$C_3H_2ReBr^+$	304	41	2	
C_3HReBr^+	303	8		
CH_2OReBr^+	296	17	5	
$CH_3OC_5H_4Re^+$	282	15	10	
$CH_3OC_5H_3Re^+$	281	34	25	
$C_5H_4COReH^+$	280	9	7	
$C_5H_4CORe^+$	279	13	7	
$ReBr^+$	266	5		
M^{2+}	253	3		
$C_5H_5Re^+$	252	14	3	
$C_5H_4Re^+$	251	8		
$C_5H_3Re^+$	250	2		
$M - CO^{2+}$, $C_5H_2Re^+$	249	3		
C_5HRe^+	248	8		
$M - 2CO^{2+}$	235	12		
$C_3H_3Re^+$	226	3		
$C_3H_2Re^+$	225	13		
C_3HRe^+	224	25		
$C_5H_4CO^+$	92	38	14	
HBr^+	80	60	30	
Br^+	79	21	4	

(continued)

TABLE 9 (continued)

Metastable transitions

m/e	Process	Neutral fragment lost
443	498 → 470 + 28	CO
419	526 → 470 + 56	2CO
411	470 → 440 + 30	CH_2O
390	445 → 417 + 28	CO
387	470 → 427 + 43	$COCH_3$
375	526 → 445 + 81	Br
362	417 → 389 + 28	CO
312	366 → 338 + 28	CO
305	470 → 378 + 92	C_5H_4CO
292	440 → 358 + 82	HBr
284	338 → 310 + 28	CO
256	310 → 282 + 28	CO
253	310 → 280 + 30	CH_2O
227	279 → 251 + 28	CO
218	358 → 279 + 79	Br

py_3 etc.) are known to undergo the expulsion of X, as well as a fragmentation of both the cyclopentadienyl ring and a ligand X, only from the ion $[C_5H_5MX_m]^+$, that is after the loss of all carbonyl groups [4]. In contrast, the molecular ions of seven-coordinate complexes of rhenium together with expulsion of carbon monoxide eliminate in parallel the substituents X and Y yielding the ions $[RC_5H_4Re(CO)_nY]^+$ and $[RC_5H_4Re(CO)_nX]^+$ ($n = 1,2$), the latter ions in some cases being of higher intensity than the ions $[M - CO]^+$.

Since a ready elimination of the CO group in preference to other π- and σ-bonded ligands is interpreted in terms of a low strength of a metal—CO bond [5], a competitive loss of the ligands X and Y (Br, I, CH_3, $COCH_3$) is due to a low (compared with metal—CO) bond strength of the metal—X and metal—Y bonds.

A probability of substituent elimination from the rhenium atom, which is defined as the ratio of the intensity of the ion $[M - X]^+$, $[M - Y]^+$ or $[M - CO]^+$ to the total intensity of these ions ($\Sigma = [M - X]^+ + [M - Y]^+ + [M - CO]^+$) depends on the nature of the substituent, as well as on the nature of its neighbours. Based on comparison of the values $[M - CO]^+/\Sigma$, $[M - Br]^+/\Sigma$ in the mass spectrum of $C_5H_5Re(CO)_2Br_2$ and the values $[M - CO]^+/\Sigma$ and $[M - CH_3]^+/\Sigma$ in the mass spectrum of $C_5H_5Re(CO)_2(CH_3)_2$, as well as the values $[M - CO]^+/\Sigma$, $[M - I]^+/\Sigma$ and $[M - CH_3]^+/\Sigma$ in the spectrum of $C_5H_5Re(CO)_2I(CH_3)$ (Table 11), the substituents are placed in the following series according to the elimination facility: Br > CO > CH_3 > I. It follows from the analysis of the mass spectrum of $C_5H_5Re(CO)_2Br(CH_3)$, however, that substitution of the bromine atom by a methyl group increases the intensity of the $[M - CO]^+$ ions compared with the $[M - Br]^+$ ions. At the same time, the insertion of the methyl group into the cyclopentadienyl ring does not affect the process of CO elimination. However, an increase in the ratio $[M - CO]^+/\Sigma$ is observed when passing to the derivatives of the seven-coordinate rhenium containing the methoxycarbonyl or iodine substituent on the ring.

It should be noted from the comparison of the mass spectra of $C_5H_5Re(CO)_2Br(CH_3)$ and $C_5H_5Re(CO)_2I(CH_3)$ that the stability of the molecular ion

TABLE 10

MASS SPECTRUM OF $\mathrm{IC_5H_4Re(CO)_2Br_2}$

Ion	*m/e*	Rel. intensity		
		50 eV	30 eV	15 eV
M^+	594	14	8	37
$M-\mathrm{CO}^+$	566	51	31	98
$M-2\mathrm{CO}^+$	538	100	75	51
$M-\mathrm{Br}^+$	513	25	30	100
$\mathrm{IC_5H_4Re}^+$	505	40	46	32
$M-\mathrm{Br}-\mathrm{CO}^+$	485	35	32	47
$\mathrm{IC_3H_2ReI}^+$	479	14	19	19
$M-\mathrm{Br}-2\mathrm{CO}^+$	457	95	100	34
$\mathrm{C_5H_5Re(CO)_2I}^+$	435	18	11	62
$\mathrm{C_5H_3Re(CO)_2I}^+$	433	17	20	32
$\mathrm{IC_3H_2ReBr}^+$	431	25	30	20
$M-2\mathrm{CO}-\mathrm{I}^+$	411	79	75	25
$\mathrm{C_5H_5Re(CO)_2Br}^+$	387	12	10	15
$\mathrm{C_5H_3Re(CO)_2Br}^+$	385	12	11	18
$\mathrm{C_5H_5ReI}^+$	379	35	27	12
$\mathrm{IC_5H_4Re}^+$	378	28	36	26
$\mathrm{C_5H_3ReI}^+$	377	36	20	20
$\mathrm{C_5H_5Re(CO)Br}^+$	359	6	5	6
$\mathrm{IC_3H_2Re}^+$	352	40	49	22
$\mathrm{ReBr_2}^+$	347	5		
$\mathrm{C_5H_5ReBr}^+$	331	24	27	10
$\mathrm{C_5H_4ReBr}^+$	330	27	40	23
$\mathrm{C_5H_3ReBr}^+$	329	54	52	21
$\mathrm{C_3H_3ReBr}^+$	305	30	18	7
$\mathrm{C_3H_2ReBr}^+$	304	67	64	19
$\mathrm{C_3HReBr}^+$	303	28	17	
$\mathrm{C_5H_4Re}^+$	251	7	6	
$\mathrm{C_5H_3Re}^+$	250	3	4	
$\mathrm{C_5H_2Re}^+$	249	12	5	
$\mathrm{C_5HRe}^+$	248	24	5	
$\mathrm{C_4H_4Re}^+$	239	6	5	
$\mathrm{C_3H_2Re}^+$	225	27	13	6
$\mathrm{C_3HRe}^+$	224	53	13	8
HI^+	128	20	26	
I^+	127	11	12	
HBr^+	80	95	100	
Br^+	79	38	48	

of the iodine compound is much higher than that of the bromide derivative. A similar tendency has already been noted by us for π-allyl complexes of iron, π-$\mathrm{AllFe(CO)_3X}$, where the stability of the molecular ion when X = I is several orders higher than when X = Cl [2]. This increase in relative intensity of the molecular ion of the iodine derivative reflects the well known stabilizing effect of iodine [6,7]. In addition to the effect of the substituents on the loss of carbon monoxide, substitution of a methyl group in the molecule results in specific fragmentation paths for these compounds.

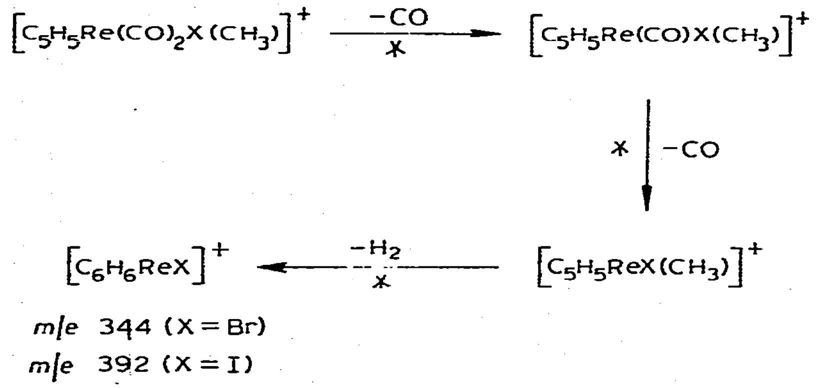
TABLE 11

THE INTENSITY RATIOS FOR $RC_5H_4Re(CO)_2XY$ ($\Sigma = [M-X]^+ + [M-Y]^+ + [M-CO]^+$)

R	X	Y	$[M-X]^+/\Sigma$		$[M-Y]^+/\Sigma$		$[M-CO]^+/\Sigma$		$[M-X]^+ + [M-Y]^+/\Sigma$	
			15 eV	50 eV	15 eV	50 eV	15 eV	50 eV	15 eV	50 eV
H	Br	Br					0.24	0.45	0.76	0.55
H	Br	CH_3	0.16	0.05	0.03	0.08	0.84	0.87	0.16	0.13
H	I	CH_3	0.02	0.02	0.14	0.20	0.85	0.78	0.15	0.22
H	CH_3	CH_3					0.87	0.80	0.13	0.20
H	I	$COCH_3$			0.22	0.34	0.56	0.31		
CH_3	Br	Br					0.24	0.42	0.76	0.58
CH_3OOC	Br	Br					0.53	0.62	0.47	0.38
I	Br	Br					0.49	0.67	0.51	0.33

The expulsion of a hydrogen molecule from the ion $[C_5H_5ReX(CH_3)]^+$, giving the ion $[C_6H_6ReX]^+$ is a common process for all σ-methyl complexes of seven-coordinate rhenium (Scheme 1). Such a process appears to be a general one for π-complexes containing a methyl group bonded to a metal atom. The molecular ion of π-indenyl—$Mo(CO)_3CH_3$ was shown [8] to eliminate three CO molecules and then a hydrogen molecule yielding the $[C_{10}H_8Mo]^+$. It has been pointed out that the loss of the hydrogen molecule is from the σ-bonded methyl group.

SCHEME 1*



The ion $[C_5H_5FeCH_3]^+$ which is formed by expulsion of three carbonyl groups from the ion $[C_5H_5Fe(CO)_2(COCH_3)]^+$ also eliminates a hydrogen molecule yielding the ion $[C_6H_6Fe]^+$ [9]. The formation of ions with 6π-electron systems, of the type $[C_6H_6M]^+$, appears to be a governing factor in this process.

Successive expulsion of three CO molecules from $C_5H_5Re(CO)_2I(COCH_3)$ results in the ion $[C_5H_5ReICH_3]^+$ which eliminates a hydrogen molecule to form the ion $[C_6H_6ReI]^+$ (*m/e* 392). This indicates that ions $[M-3CO]^+$ present in

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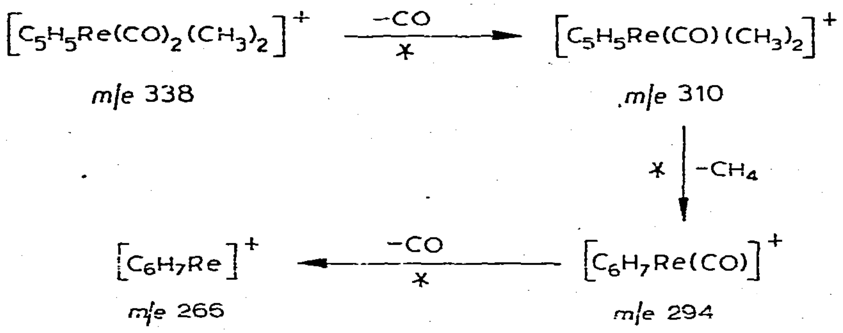
* Here and in the following schemes, the asterisks denote degradation routes identified through the respective metastable peaks.

the mas spectrum of $C_5H_5Re(CO)_2I$ $(COCH_3)$ and $[M - 2CO]^+$ in the spectrum of $C_5H_5Re(CO)_2$ (CH_3) are structurally similar.

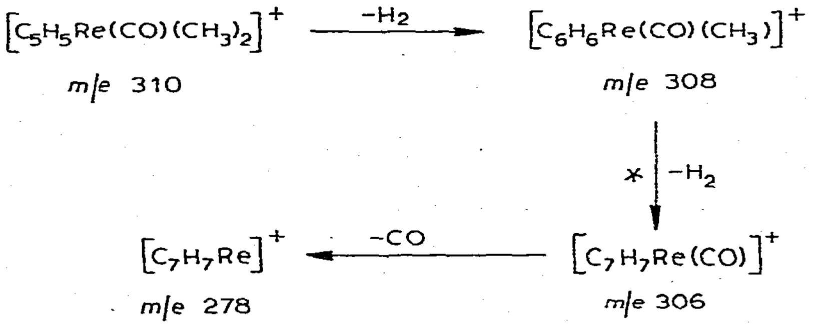
The presence of two methyl groups σ-bonded to the metal atom results in alternative fragmentation paths for the molecular ion of $C_5H_5Re(CO)_2(CH_3)_2$. A successive elimination of carbonyl groups from the molecular ion, which is a typical process for carbonyl complexes, is absent in this case. Instead a consecutive expulsion of CO, CH_4 and CO is observed which leads to the base ion $[C_6H_7Re]^+$ in the spectrum. A loss of the second carbonyl group proceeds, therefore, only after elimination of a methane molecule from the ion $[M - CO]^+$ (Scheme 2).

SCHEME 2



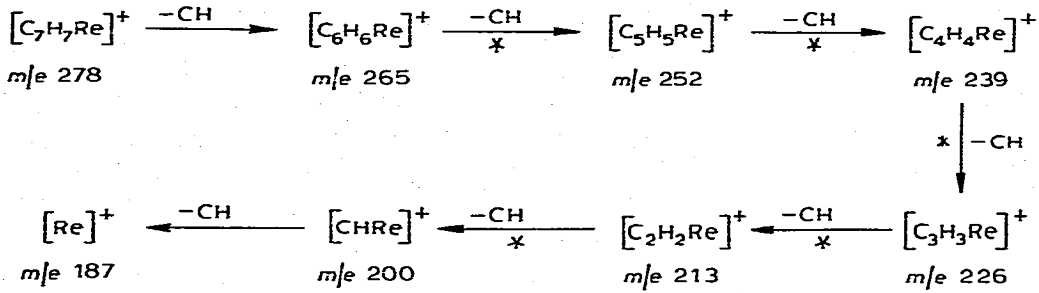
Further degradation of $[C_6H_7Re]^+$ results in the ions $[C_6H_6Re]^+$ (*m/e* 265), $[C_6H_5Re]^+$ (*m/e* 264), $[C_6H_4Re]^+$ (*m/e* 263) and $[C_6H_3Re]^+$ (*m/e* 262). Another competitive fragmentation path of the ion $[C_5H_5Re(CO)(CH_3)_2]^+$ (*m/e* 310) consists of successive elimination of two hydrogen molecules with the formation of the ions with *m/e* 308 and *m/e* 306 (Scheme 3).

SCHEME 3



Decarbonylation of the ion $[C_7H_7Re(CO)]^+$ leads to the ion $[C_7H_7Re]^+$ further fragmentation of which consists of a stepwise elimination of CH (Scheme 4).

SCHEME 4



The ions $[C_6H_6Re]^+$, formed from the molecular ions of $C_5H_5Re(CO)_2(X)(CH_3)$, undergo a similar degradation to that in Scheme 4. One can assume that a consecutive loss of methine groups proceeds from the linear form of the ion $[C_7H_7Re]^+$. It is to be noted that a similar fragmentation path is not realized in the mass spectrum of $C_5H_5Re(CO)_3$ [9] where the ion $[C_5H_5Re]^+$ degrades due to expulsion of acetylene and hydrogen molecules yielding the $[C_3H_3Re]^+$ and $[C_5H_3Re]^+$ ions, respectively. A different degradation of the ions $[C_5H_5Re]^+$, formed in the course of fragmentation of the $C_5H_5Re(CO)_3$ and σ-methyl complexes of seven-coordinate rhenium, suggests they are structurally dissimilar. The occurrence of the ions $[C_nH_nRe]^+$ ($n = 1$-7) in the mass spectrum is thus witness to the presence of a methyl substituent σ-bonded to the rhenium atom in the parent molecule.

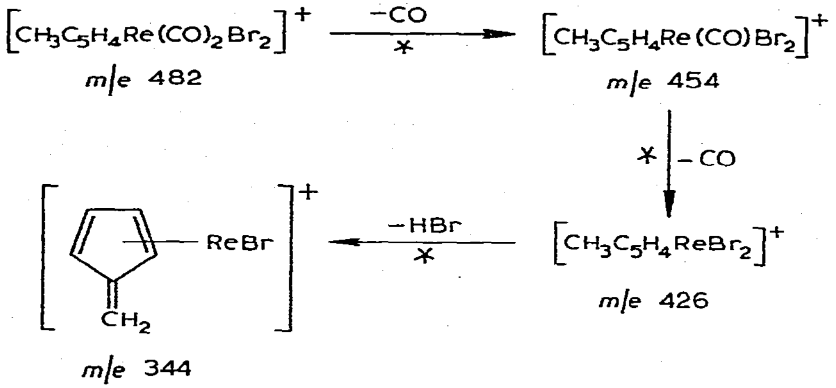
The molecular ions of hydrides, $C_5H_5Re(CO)_2BrH$ and $C_5H_5Re(CO)_2IH$ decompose only in the manner due to expulsion of the CO groups. A competitive elimination of a hydrogen atom is not observed. The loss of a H atom proceeds only from the ion $[C_5H_5ReXH]^+$. A similar behaviour of transition metal hydrides has earlier been noted by King [9] in the case of $C_5H_5WH(CO)_3$ where the elimination of a CO molecule from the molecular ion is followed by the loss of the hydrogen atom. The presence of the abundant *m/e* 336 peaks in the spectra of hydrides studied is apparently due to a small impurity, the more volatile cyclopentadienylrheniumtricarbonyl.

The signal due to the ion $[C_5H_5Re(CO)_2I]^+$ (*m/e* 435) in the spectrum of $C_5H_5Re(CO)_2I(HgCl)$ is the highest *m/e* ratio, while the M^+ peak is not observed. This is witness to a low bond strength for the Re—Hg bond. It should be noted that the ions $[M - Hal]^+$ containing the metal—metal bond were present in the mass spectra of $C_5H_5Mo(CO)_3HgCl$ [10] and $C_5H_5Mo(CO)_3HgI$ [11].

As was observed for the corresponding molybdenum complexes, a migration of the chlorine atom to the metal resulting in the ions $[C_5H_5ReCl]^+$ (*m/e* 287) and $[C_5H_3ReCl]^+$ (*m/e* 285) is a characteristic feature of fragmentation of the $C_5H_5Re(CO)_2IHgCl$ molecule.

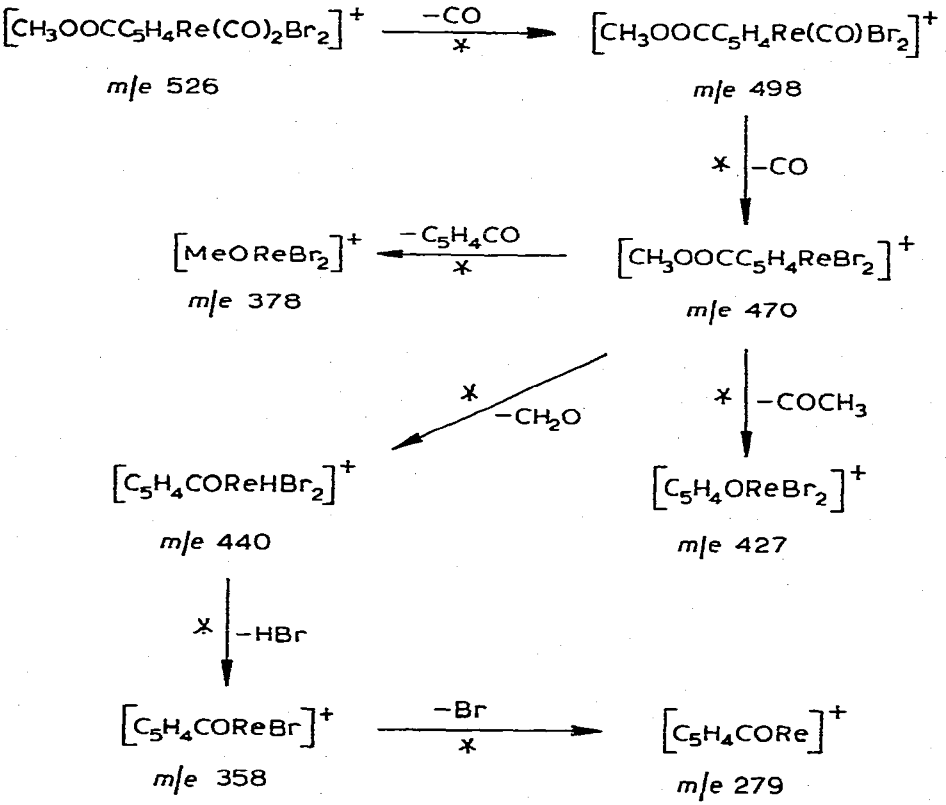
It follows from the data in Table 11 that the substitution of a methyl group onto the cyclopentadienyl ring practically does not affect elimination of the first CO group and the bromine atom from the molecular ion. However, the presence of the methyl group gives rise to expulsion of a hydrogen bromide molecule from the ion $[M - 2CO]^+$ which results in the most abundant ion $[CH_2C_5H_4ReBr]^+$ (*m/e* 344) (Scheme 5). The latter appears to have the fulvene structure similar to that proposed by us earlier for the ion $[M - HX]^+$ in the mass spectrum of $CH_3C_5H_4TiX_3$ ($X = Cl, Br$).

SCHEME 5



The presence of the methoxycarbonyl group on the cyclopentadienyl ring leads to certain specific features in the fragmentation pattern of the molecular ion of $CH_3OOCC_5H_4Re(CO)_2Br_2$ under electron impact (Scheme 6). Together with abundant processes of elimination of the CO groups and the bromine atom the loss of the methoxyl radical is observed from the molecular ion. A known-

SCHEME 6



process of migration of the methoxyl group to the metal atom leads to the ion $[CH_3OReBr_2]^+$ with *m/e* 378 [12]. The loss of HBr from the latter yields the ion $[CH_2OReBr]^+$ (*m/e* 296). The elimination of formaldehyde described earlier for ferrocenyl ester [12] leads in this particular case to the ion $[C_5H_4COReHBr_2]^+$ (*m/e* 440) further decomposition of which results in the ion $[C_5H_4Re]^+$ (*m/e* 251). A similar process of CH_2O elimination is also found from the ion $[CH_3OOC{-}C_5H_4Re]^+$.

An unusual expulsion of the acetyl group from the $[M - 2CO]^+$ ion should be emphasized. The ion $[C_5H_4OReBr_2]^+$ with *m/e* 427 formed thereby further loses the oxygen atom yielding the ion $[C_5H_4ReBr_2]^+$ (*m/e* 411).

The presence of the abundant ions $[IC_5H_4ReI]^+$ (*m/e* 505), $[IC_3H_2ReI]^+$ (*m/e* 479) and $[C_5H_5Re(CO)_2I]^+$ (*m/e* 435) is characteristic of the mass spectrum of $IC_5H_4Re(CO)_2Br_2$. The formation of the ions mentioned appears to be due to substitution of bromine for iodine, this process taking place in the gas phase.

Experimental

The mass spectra were run on the mass spectrometer MX1303 provided with a direct inlet system at 30-90° C; the temperature of the ionizing chamber was 150°C. The ionizing voltage was 50, 30 and 15 eV.

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